Table VI. Experimental Data for 9-(Dinitromethyl)-9-alkoxyfluorenes (2)[a]

compd	yield, %	mp,[b] °C	NMR[c] ($CDCl_3$), δ
2-Me	68	92	2.84 (3 H, s), 6.82 (1 H, s), 7.2–7.7 (8 H, m)
2-Et	46	113	1.02 (3 H, t), 2.96 (2 H, q), 6.86 (1 H, s), 7.2–7.7 (8 H, m)
2-Pr	6.5	94	0.9 (6 H, dd), 3.2 (1 H, m), 6.9 (1 H, s), 7.4 (8 H, m)
2-Tf	43	84–85	3.26 (2 H, q), 6.9 (1 H, s), 7.5 (8 H, m)

[a] All four compounds gave satisfactory C, H, N, and F analyses. [b] Uncorrected, taken on Fischer-Johns apparatus. [c] Taken on Varian HA-100. The internal standard was Me_4Si.

branching of the alkyl chain leads to decreased acidity probably because of steric inhibition of reasonance by forcing the nitro groups out of the plane.[17] However, in spite of the large difference in the steric size of the substituents, the pK_a values of the four substrates fall into a narrow range. Since the demand for planarity in the carbanion renders it more sensitive to steric effects when compared to the neutral molecule, it is unlikely that the observed lack of sensitivity to steric effects results from a mutual cancellation of identical effects exerted on the acid and its conjugated base. This is consistent with our previous assumption that the dinitromethide moiety is sterically affected mainly by the first atom of the added nucleophile. The observed pK_a's of the substrates 2 can be correlated with the electronic effects of the substituents.

Experimental Section

Materials. 9-Alkoxy-9-(dinitromethyl)fluorenes (2-Me, -Et, -Pr, and -Tf). All four compounds were prepared by the addition of the alkoxide (4.5 mmol) in 30 mL of the parent alcohol to 9-(dinitromethylene)fluorene (1.86 mmol). After gentle heating for 10 min, during which the solid is dissolved, the reaction mixture is cooled by adding ice directly to the reaction vessel and is gently acidified by cold diluted HCl. Extraction with ether, drying over Na_2SO_4, and evaporation of the solvent yielded a white solid which was recrystallized from petroleum ether. The experimental data are given in Table VI.

The solutions for the kinetic experiments were composed of 90% doubly distilled water and 10% dioxane (by volume) purified according to a published procedure.[18] The buffering agents (starting from low to high pH's) were chloroacetic acid, phthalic acid, formic acid, acetic acid, dihydrogen phosphate, borax, and sodium hydroxide.

Kinetics. The hydrolysis of 2 was followed spectroscopically. In each of the buffers used, the reaction was first monitored with each of the substates by repetitive scanning in the UV–vis region (Perkin-Elmer 402 spectrophotometer), and the actual kinetics were observed by following the increase in the absorbance of fluorenone at 259 nm with a Gilford 2400 spectrophotometer. The spectrophotometer was attached to a PDP 11/40 minicomputer for data handling. The buffered solutions were preincubated (ca. 0.5 h) in the cell compartment which was thermostated to 25 ± 0.1 °C. The substrates were injected (10 μL) into the UV cell as a concentrated dioxane solution, and the monitoring started immediately after a rapid mixing. Each data point in the tables is an average of four to seven different experiments.

Registry No. 2 (R = *i*-Pr), 82615-41-6; 2 (R = Et), 82615-42-7; 2 (R = Me), 82615-43-8; 2 (R = Tf), 82615-44-9; 9-(dinitromethylene)fluorene, 25945-85-1.

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Cyclopropanation of α,β-Unsaturated Carbonyl Compounds and Nitriles with Diazo Compounds. The Nature of the Involvement of Transition-Metal Promoters

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In the presence of molybdenum hexacarbonyl or molybdenum(II) acetate, ethyl diazoacetate and α-diazoacetophenone react with α,β-unsaturated carbonyl compounds and nitriles to form derivative cyclopropane and vinyl CH insertion products. In the absence of these promoters or in the presence of catalytic amounts of pyridine, 2-pyrazolines are the major or sole reaction products. Kinetic investigations for reactions between ethyl diazoacetate and α,β-unsaturated esters and nitriles in the presence of $Mo(CO)_6$, $Mo_2(OAc)_4$, or pyridine demonstrate the absence of any significant influence by these molybdenum promoters or pyridine on the rates and activation parameters for ethyl diazoacetate decomposition. Representative 1-pyrazolines have been synthesized and observed to undergo dinitrogen extrusion without apparent influence by molybdenum promoters. The composite results suggest that these molybdenum promoted reactions occur by dipolar cycloaddition of diazocarbonyl compounds to α,β-unsaturated systems and that the derivative 1-pyrazoline intermediates undergo dinitrogen extrusion to form the observed cyclopropane and vinyl CH insertion products. Molybdenum promoters function to inhibit competitive tautomerization of the initially formed cycloaddition products. The relative effectiveness of a broad selection of transition-metal compounds in directing reactions between ethyl diazoacetate and α,β-unsaturated esters and nitriles to cyclopropane products is described. The cycloaddition/dinitrogen extrusion pathway is presented as a viable mechanism for cyclopropanation of α,β-unsaturated systems by diazo compounds, even for reactions performed in the presence of traditional cyclopropanation catalysts.

Diazo compounds readily undergo 1,3-dipolar addition to α,β-unsaturated carbonyl compounds and nitriles.[1–3] The resulting 1-pyrazoline, if formed from an activated olefin or a diazocarbonyl compound that possesses an α

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Table I. Product Yields from $Mo(CO)_6$- and $Mo_2(OAc)_4$-Promoted Reactions of α-Diazoacetophenone and Ethyl Diazoacetate with Representative α,β-Unsaturated Carbonyl Compounds and Nitriles[a]

			$Mo(CO)_6$[b]			$Mo_2(OAc)_4$[c]		
R	R'	Z	1, % (*E*/*Z*)[d]	2, %	3, %	1, % (*E*/*Z*)[d]	2, %	3, %
C_6H_5	H	COOEt	72 (1.7)	<2	10			
EtO	H	COOEt	31 (1.6)	10	50	27 (1.5)	6	58
C_6H_5	CH_3	COOMe	85 (1.9)	4	0			
EtO	CH_3	COOMe	80 (1.4)	10	3	71 (1.4)	17	2
C_6H_5	H	CN	68 (2.2)	3	28			
EtO	H	CN	46 (1.1)	13	35	42 (1.1)	5	40
C_6H_5	CH_3	CN	58 (1.2)	4	0			
EtO	CH_3	CN	80 (0.70)	8	0	72 (0.79)	4	0
C_6H_5	H	$COCH_3$[e]	52 (2.4)	3	0			
EtO	H	$COCH_3$				32 (1.5)	4	*f*

[a] Reactions were performed at 65 °C in the olefinic component that was employed as the reaction solvent. Averaged results from duplicate runs are reported. [b] 1.0 mol %, based on diazocarbonyl compound, except for reactions with ethyl acrylate for which 15 mol % $Mo(CO)_6$ was employed. [c] 0.50 mol %, based on diazocarbonyl compound. [d] The (*E*/*Z*) notation (*E*:trans relationship for groups of higher priority) is employed to avoid confusion in assignment of isomeric cyclopropanes. [e] Reaction performed with methyl vinyl ketone (10% v/v) in toluene at 50 °C. [f] Not determined.

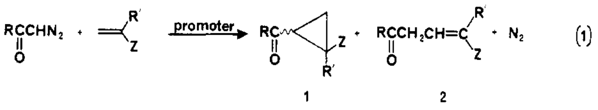
hydrogen, is subject to rapid tautomerization that produces normally isolable 2-pyrazoline products.[4,5] If the reactants possess α substituents, cyclopropane and vinyl CH insertion products are formed by nitrogen extrusion from the initially formed 1-pyrazoline.[6] Cyclopropane formation is rarely observed to compete effectively with tautomerization.[7,8]

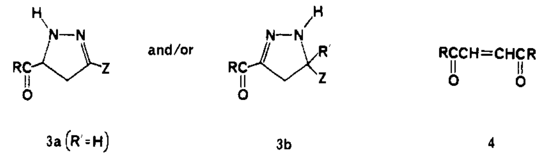
Cyclopropane formation by catalytic decomposition of diazo compounds is well-established for alkenes that can serve as nucleophilic reactants toward electrophilic metal carbenes, and an expanding group of catalysts is being developed for this transformation.[9-11] However, electrophilic metal carbenes do not undergo addition to the carbon-carbon double bond of α,β-unsaturated carbonyl compounds or nitriles, and alternate modes of reaction occur in preference to cyclopropanation.[12-14] Stable α-methoxyphenylcarbenes of metals in the chromium triad undergo cyclopropane formation with α,β-unsaturated carbonyl compounds,[15] but similar catalytic transformations involving nucleophilic metal carbenes have not been demonstrated.

We have recently reported that molybdenum hexacarbonyl effectively promotes the cyclopropanation of α,β-unsaturated esters and nitriles with diazocarbonyl compounds.[16] In the absence of the molybdenum promoter, the primary reaction products are 2-pyrazolines, and cyclopropane formation is not substantially competitive under conditions identical with those employed for reactions performed in the presence of $Mo(CO)_6$. Consideration of the facility with which molybdenum binds dinitrogen[17] and the known reactivity of nucleophilic molybdenum-carbene complexes toward α,β-unsaturated esters[15,18] suggests that catalytic involvement of $Mo(CO)_6$ could occur by molybdenum-promoted decomposition of 1-pyrazolines, by nucleophilic molybdenum-carbene addition, or by yet another pathway. We now report the full details of our investigation.

Results

Molybdenum-Promoted Reactions. Diazocarbonyl compounds, of which α-diazoacetophenone and ethyl diazoacetate are representative, undergo decomposition in the presence of catalytic amounts of $Mo(CO)_6$ to produce cyclopropane and vinyl CH insertion products by reactions with α,β-unsaturated carbonyl compounds and nitriles (eq 1). Pyrazoline (3) and dimeric carbenoid products (4) are formed competitively but, normally, in low yield. With only one system, that of ethyl diazoacetate with ethyl acrylate in the absence of promoter or in the presence of less than 2 mol % of $Mo(CO)_6$, was the presence of the 1-pyrazoline cycloaddition product indicated. In the course of this investigation, molybdenum(II) acetate was discovered to be similarly effective for cyclopropane formation. Product yields from reactions promoted by $Mo(CO)_6$ and by $Mo_2(OAc)_4$ with representative α,β-unsaturated carbonyl compounds and nitriles are reported in Table I. Not reported in this table are results from $Mo(CO)_6$-promoted reactions with ethyl crotonate and acrolein, from which exceptionally complex reaction mixtures were obtained





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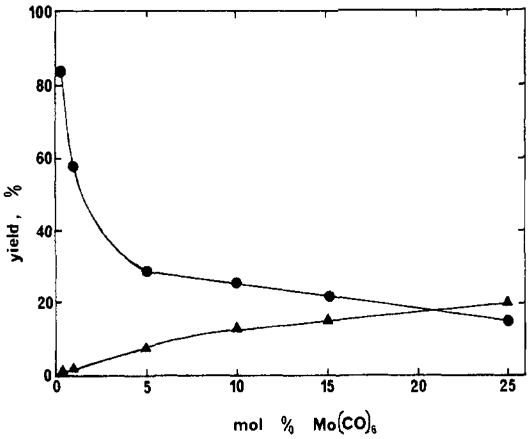


Figure 1. Effect of mole percent Mo(CO)$_6$ on product yields [(●) 2-benzoyl-1-methylcyclopropanenitrile, (▲) acetophenone] in reactions of α-diazoacetophenone with methacrylonitrile.

that included only minor amounts of cyclopropane products.

Notably, $Mo_2(OAc)_4$ and Mo(CO)$_6$ are comparable in their ability to promote the formation of cyclopropane products. The relative amount of vinyl CH insertion products is generally greater for reactions with ethyl diazoacetate than with α-diazoacetophenone and, with one exception, greater in Mo(CO)$_6$-promoted reactions than in $Mo_2(OAc)_4$-promoted reactions. Under the reaction conditions employed for these transformations, carbene dimers, diethyl fumarate and diethyl maleate from ethyl diazoacetate and dibenzoylethylene from α-diazoacetophenone, are observed, but the extent of their production is usually less than 4% of the reactant diazocarbonyl compound. Cyclopropane isomer ratios are not observed to be sensitive to either the amount or nature of the molybdenum compound that is employed.

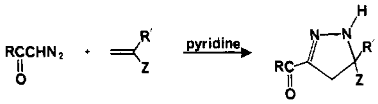
The yields reported in Table I were obtained from reactions performed under standard conditions and are exceptionally sensitive to the amount of Mo(CO)$_6$ that is employed. For example, α-diazoacetophenone reacts with acrylonitrile in the presence of 0.2 mol % Mo(CO)$_6$ to produce 1 (46%), **2** (2%), and **3b** (50%). In the presence of 1.0 mol % Mo(CO)$_6$, 1 (68%), **2** (3%), and **3b** (28%) are formed. The pyrazoline byproduct is completely absent when 15 mol % of Mo(CO)$_6$ is employed, and 1 (83%) and **2** (4%) are produced together with acetophenone (3%) as the sole identifiable products. In the absence of the molybdenum promoter, pyrazoline **3b** (R = Ph, R′ = H) is the major product (78% yield), and only relatively minor amounts of cyclopropane (17%) and insertion (>1%) products are formed. Similar behavior characterizes reactions of α-diazoacetophenone with ethyl acrylate. In contrast, 2-pyrazoline production is not the limiting factor in reactions of α-diazoacetophenone with methacrylonitrile. In this case, increasing the mole percentage of Mo(CO)$_6$ produces a dramatic decrease in the yield of cyclopropane products and concomitant formation of acetophenone (Figure 1). Only minor amounts of **3b** (<2%) are observed at the low [Mo(CO)$_6$]/[PhCOCHN$_2$] ratios. In the absence of Mo(CO)$_6$, 1 (R′ = CH$_3$) is produced in less than 10% yield.

Modification of Mo(CO)$_6$ by substitution of phosphine or amine ligands for carbon monoxide produces no apparent advantage for cyclopropane formation (Table II). Basic reagents such as triphenylphosphine or pyridine facilitate the formation of 2-pyrazoline products. Indeed, the use of these bases, particularly pyridine, offers the most suitable method for the synthesis of 2-pyrazolines from diazocarbonyl compounds and α,β-unsaturated esters and nitriles in quantitative yield (eq 2).[19] Furthermore, re-

Table II. Product Yields from Reactions of Ethyl Diazoacetate with Methacrylonitrile in the Presence of Molybdenum-Based Compounds[a]

promoter[b]	addend[c]	1,[d] %	2, %	3b, %	4, %
Mo(CO)$_6$		80	8	0	2
Mo(CO)$_6$	CO	67	<2	12	1
Mo(CO)$_6$	Ph$_3$P	0	0	100	0
Mo(CO)$_4$(Ph$_3$P)$_2$		81	8	9	1
Mo(CO)$_4$(Ph$_3$P)$_2$	CO	20	2	50	2
Mo(CO)$_4$(pip)$_2$[e]		0	0	98	0
Mo(CO)$_4$(Ph$_3$P)(pip)[e]		63	<2	10	<1
Mo(N$_2$)$_2$(dppe)$_2$[f]		15	<1	84	0
pyridine[g]		0	0	100	0
none		<10	<1	50	<1

[a] Reactions were performed at 65 °C with methacrylonitrile (50% v/v) in benzene. [b] Mo(CO)$_6$ was employed at 1.0 mol %, based on ethyl diazoacetate. Modified molybdenum compounds were employed at 5.0 mol %. [c] Carbon monoxide (1 atm) was maintained above the reaction solution. Triphenylphosphine (2.0 equiv, based on ethyl diazoacetate) was employed. [d] Product isomer ratio was independent of the molybdenum promoter. [e] pip = piperidine. [f] dppe = bis(1,2-diphenylphosphino)ethane. [g] 5.0 mol % in benzene.



(2)

actions performed with molybdenum carbonyl catalysts under an atmosphere of carbon monoxide generally resulted in increased production of 2-pyrazolines. In separate experiments, 2-pyrazolines were shown to be stable toward decomposition to derivative cyclopropanes in the presence of Mo(CO)$_6$ even at higher temperatures and longer reaction times than those employed for cyclopropane formation.

Product yields from reactions of methacrylonitrile with α-diazoacetophenone using 1.0 mol % Mo(CO)$_6$ were constant (1, 58 ± 2%) so long as the molar ratio of methacrylonitrile to diazo compound was maintained at or higher than 6.0. Dilution of methacrylonitrile with toluene, benzene, or acetonitrile beyond a volume ratio of 1.0 resulted in decreased product yields when the molar ratio of methacrylonitrile to α-diazoacetophenone was maintained at 6.0. The use of methacrylontrile and α-diazoacetophenone in stoichiometric amounts resulted in only an 11% yield of cyclopropane products when this reaction was performed in toluene. 2-Pyrazoline production was facilitated with the use of polar solvents: acetonitrile (1, 58%; **3b**, 3%), ethyl acetate (1, 49%; **3b**, 5%), nitromethane (1, 50%; **3b**, 15%), and *N,N*-dimethylformamide (1, 21%; **3b**, 54%) at a volume ratio of 1.0 and a molar ratio of methacrylonitrile to α-diazoacetophenone of 15.

Reaction Kinetics. In order to assess the nature of the involvement of molybdenum compounds in reactions of diazocarbonyl derivatives with α,β-unsaturated carbonyl compounds and nitriles, we undertook a thorough kinetic study of the rate of decomposition of ethyl diazoacetate with four representative activated olefins. Reactions were observed to be first order in ethyl diazoacetate and first order in the activated olefinic substrate. The effects of both Mo(CO)$_6$ and $Mo_2(OAc)_4$ on the rates for these re-

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[19] Prior methods, using a wide variety of reaction conditions and catalysts, have not achieved consistently high yields of 2-pyrazoline products in comparable systems.[5]

Table III. Kinetic Results from Reactions of Ethyl Diazoacetate with Representative α,β-Unsaturated Esters and Nitriles in the Presence of Pyridine, $Mo(CO)_6$, and $Mo_2(OAc)_4$[a]

olefin[b] (mol/L)	promoter[c]	10^5k, $M^{-1}\ s^{-1}$ (52.0 °C)[d]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$H_2C{=}CHCOOEt$ (2.4)	5.0% pyridine	26.2	11.5	−39.2
	2.5% $Mo(CO)_6$	26.1	11.9	−38.9
	0.5% $Mo_2(OAc)_4$	28.8	12.2	−38.6
$H_2C{=}CHCN$ (10.6)	5.0% pyridine	17.1	11.5	−49.9
	10% $Mo(CO)_6$	17.7	11.8	−46.8
	0.5% $Mo_2(OAc)_4$	17.5	11.3	−47.2
$H_2C{=}C(CH_3)COOMe$ (6.6)	5.0% pyridine	2.92	14.5	−25.6
	10% $Mo(CO)_6$	3.10	14.3	−25.0
	0.5% $Mo_2(OAc)_4$	3.37	14.6	−25.1
$H_2C{=}C(CH_3)CN$ (8.4)	5.0% pyridine	0.55	14.9	−36.8
	5.0% $Mo(CO)_6$	0.56	15.7	−35.9
	0.5% $Mo_2(OAc)_4$	0.76	15.5	−35.5

[a] Reactions were performed with ethyl diazoacetate (0.66 M) except for ethyl acrylate transformations with ethyl diazoacetate (0.48 M). Pseudo-first-order kinetics were observed through 2 half-lives. [b] The olefin was dissolved in benzene. [c] Mol %, based on ethyl diazoacetate. In the absence of any promoter, ethyl acrylate reacted with ethyl diazoacetate at 52.0 °C with $k = 27.2 \times 10^{-5}\ M^{-1}\ s^{-1}$, and methacrylonitrile reacted with ethyl diazoacetate at 52.0 °C with $k = 0.52 \times 10^{-5}\ M^{-1}\ s^{-1}$. [d] Multiple runs exhibited deviations of less than 5% in the reported values.

actions were determined at a minimum of four different temperatures, and product yields similar to those reported in Table I were obtained. Pyridine was employed to monitor the rates for cycloaddition of ethyl diazoacetate to the unsaturated ester or nitrile in reactions performed without molybdenum promoters, and only the corresponding 2-pyrazolines were produced in these reactions. The progress of these reactions was conveniently followed by determining the rate of loss of the diazo compound with time, and, in selected separate analyses, rates for cyclopropane formation were found to be identical with the corresponding rates for ethyl diazoacetate consumption. The composite kinetic results are reported in Table III. In all cases, neither $Mo_2(OAc)_4$ nor $Mo(CO)_6$ affects the rates or activation parameters for ethyl diazoacetate decomposition to any significant extent despite the disparity in product formation.

The use of pyridine in amounts ranging from 0 mol % to 42 mol %, based on ethyl diazoacetate, did not affect the rate for cycloaddition of ethyl diazoacetate to ethyl acrylate or methacrylonitrile. However, the use of $Mo_2(OAc)_4$ in amounts ranging from 0.5 mol % to 10.0 mol % produced an observable increase in the rate for ethyl diazoacetate decomposition that was less evident when $Mo(CO)_6$ was employed (Figure 2). Decreased cyclopropane production (Figure 3) and corresponding formation of diethyl fumarate and diethyl maleate accompanied these rate increases, which signified an alternate pathway for ethyl diazoacetate decomposition. In the limit as the molybdenum(II) acetate concentration approaches zero, the rate for ethyl diazoacetate decomposition approaches that observed from reactions performed in the presence of $Mo(CO)_6$ or pyridine.

In the absence of the α,β-unsaturated substrate, $Mo(CO)_6$ and $Mo_2(OAc)_4$ catalyzed the formation of diethyl fumarate and diethyl maleate from ethyl diazoacetate under reaction conditions similar to those employed for these kinetic determinations. The optimum yield of these coupled products, obtained from separate experiments, was 32% from reactions promoted by $Mo(CO)_6$ and 56% from reactions promoted by $Mo_2(OAc)_4$, and diethyl maleate was the dominant isomer: 6.5:1 for $Mo(CO)_6$, 8:1 for $Mo_2(OAc)_4$.[20]

1-Pyrazoline Decomposition. In view of the absence of a kinetic distinction between molybdenum-promoted

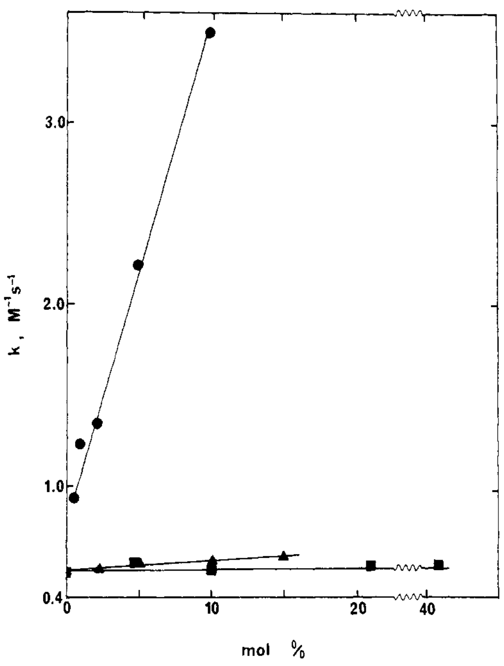

Figure 2. Dependence of rate constants for ethyl diazoacetate decomposition on the amount of promoter in reactions of ethyl diazoacetate with methacrylonitrile at 52 °C: $Mo_2(OAc)_4$ (●), $Mo(CO)_6$ (▲), pyridine (■).

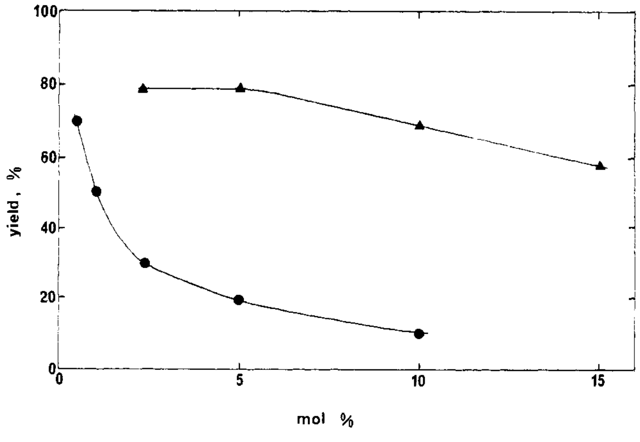

Figure 3. Dependence of the yield of ethyl 2-cyano-2-methylcyclopropanecarboxylate on the amount of promoter in reactions of ethyl diazoacetate with methacrylonitrile at 52 °C: $Mo_2(OAc)_4$ (●), $Mo(CO)_6$ (▲).

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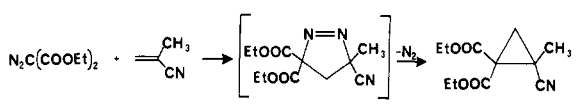
[20] Attempts to utilize $Mo(CO)_6$ and $Mo_2(OAc)_4$ for intramolecular coupling of bis(diazocarbonyl) compounds[21] were unsuccessful.

Table IV. Product Yields from Reactions of Ethyl Diazoacetate with Methacrylonitrile and Ethyl Acrylate or Acrylonitrile in the Presence of Selected Transition-Metal Compounds[a]

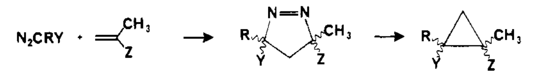
		methacrylonitrile			ethyl acrylate/acrylonitrile			
promoter	mol %[b]	1, %	2, %	3, %	EA/AN[c]	1, %	2, %	3, %
Cp_2ZrCl_2	1.0	74	7	0	EA	30	8	42
$V(CO)_6$	0.5	86	1	4	EA	26	47	8
$C_6H_6Cr(CO)_3$	1.0	22	1	55	AN	0	0	93
$Mo(CO)_6$	1.0[d]	80	8	0	EA	31	10	50
$Mo_2(OAc)_4$	0.5	72	4	0	EA	27	6	58
$Mn_2(CO)_{10}$	1.0	40	3	45	EA	8	2	23
$Re_2(CO)_{10}$	1.0	0	0	80	EA	0	0	100
$Fe(CO)_5$	4.0[e]	63	3	0	EA	45	8	42
$Fe_2(CO)_9$	4.0[e]	46	2	0	AN	33	5	55
$Fe_3(CO)_{12}$	2.0[e]	27	1	8	AN	22	3	63
$Ru_3(CO)_{12}$	1.4	6	t	0[f]	AN	5	Tr	93
$Os_3(CO)_{12}$	1.0	44	2	41	AN	39	6	52
$Ir_4(CO)_{12}$[g]	1.0	0	0	100	EA	0	0	92
$(Ph_3P)_2Ir(CO)Cl$	1.0	0	0	85	EA	0	0	60

[a] Reactions were performed at 65 °C in the olefinic compound or with the olefinic compound in benzene (50% v/v). [b] Based on ethyl diazoacetate. [c] EA = ethyl acrylate, AN = acrylonitrile. [d] For reaction with ethyl acrylate, 15 mol % was employed. [e] Amount employed to obtain optimum yield of products; lower yields are observed at either higher or lower mole percentage of these promoters. [f] Diethyl maleate and fumarate were observed (20% yield). [g] Less than 5% yield of volatile products was observed with either system in reactions performed in the presence of $Co_2(CO)_8$ and $CpCo(CO)_2$.

cyclopropane formation and pyridine-promoted 2-pyrazoline production, the effect of $Mo(CO)_6$ and $Mo_2(OAc)_4$ on the decomposition of representative 1-pyrazolines was investigated. Attempted syntheses of the 1-pyrazoline derived from the reaction between diethyl diazomalonate and methacrylonitrile only resulted in a complex product mixture from which cyclopropane formation was evident (eq 3). Use of ethyl diazopropionate with methacrylonitrile gave the corresponding 1-pyrazolines together with derivative cyclopropane products (eq 4: Y = COOEt, R = CH_3, Z = CN). Comparative decomposition of 5 at 25 °C in the presence and absence of $Mo(CO)_6$ or $Mo_2(OAc)_4$ (10 mol %) produced 6 as the dominant product at the same rate and with the same isomer ratio (*E*/*Z* = 0.78). Similarly, decomposition of 5 (R = H, Y = Ph, Z = COOMe), prepared by dipolar addition of phenyldiazomethane to methyl methacrylate, at 25 °C in the presence and absence of these molybdenum promoters (10 mol %) gave identical results, both in relative rates for 1-pyrazoline decomposition and in the cyclopropane isomer ratio (*E*/*Z* = 0.50). Only when an equivalent amount of $Mo(CO)_6$ or $Mo_2(OAc)_4$, relative to 5, was employed did a moderate degree of rate enhancement, a factor of 1.2–1.3, become evident but, even in these cases, product yields and cyclopropane isomer ratios did not vary from those obtained from reactions performed in the absence of these molybdenum compounds.



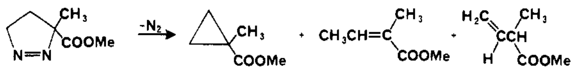
(3)



(4)

5 6

Thermal decomposition of 3-methyl-3-(carbomethoxy)-1-pyrazoline (7) at temperatures ranging from 90 to 155 °C gave a mixture of cyclopropane and olefinic products (eq 5) whose composition corresponded to that previously reported for the pyrolysis of 7.[22] However, neither $Mo(CO)_6$ nor $Mo_2(OAc)_4$ affected the rate of decomposition of 7, product yields, or the product ratios.

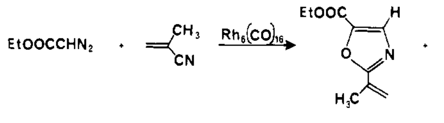


(5)

7 8 9 10

Molybdenum Alternatives for Cyclopropane Formation. Investigations of the effectiveness of transition-metal compounds other than those of molybdenum in promoting cyclopropane formation from reactions of ethyl diazoacetate with α,β-unsaturated carbonyl compounds and nitriles provided the results that are described in Table IV. Comparative results with $W(CO)_6$ and $Cr(CO)_6$ have been reported.[16]

As is evident in these results, Cp_2ZrCl_2 and $V(CO)_6$ are at least as effective as molybdenum compounds in diverting the reaction course from 2-pyrazoline production; $Mn_2(CO)_{10}$ is much less effective, and neither rhenium nor iridium carbonyls exhibit any activity for cyclopropane formation. Iron carbonyls exhibit a spectrum of activities, with $Fe(CO)_5$ being the most effective for cyclopropane formation, but none of these compounds catalyze the decomposition of ethyl diazoacetate in a manner that is different from that described for $Mo(CO)_6$ or $Mo_2(OAc)_4$. In contrast, transition-metal compounds that are active for catalytic cyclopropanation with relatively nucleophilic olefins do not operate effectively with α,β-unsaturated carbonyl compounds and nitriles. For example, 2-pyrazoline and both diethyl maleate and diethyl fumarate were obtained from the reaction of ethyl acrylate with ethyl diazoacetate in the presence of 1.0 mol % $Rh_6(CO)_{16}$, and with acrylonitrile 2-pyrazoline 3b was produced in 82% yield along with 5% cyclopropane products and 8% of diethyl maleate and diethyl fumarate. With methacrylonitrile, however, oxazole formation (eq 6) was observed



(6)

(20%) in addition to cyclopropane products (18%) and diethyl fumarate and maleate (22%); pyrazoline 3b was not observed.[23] The oxazole derived from ethyl diazo-

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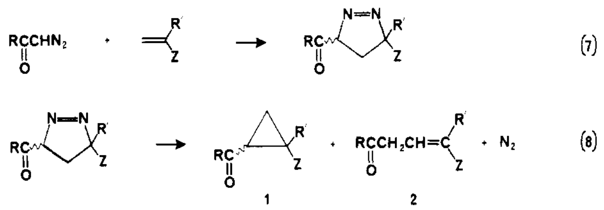
(21) Kulkowit, S.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1978**, 1069.

(22) McGreer, D. E.; Masters, I. M. E. *Can. J. Chem.* **1969**, *47*, 3975.

(23) Oxazole formation is also characteristic of reactions performed in the presence of $Rh_2(OAc)_4$, $[Rh(CO)_2Cl]_2$, and copper compounds that are commonly employed as cyclopropanation catalysts.

Scheme I



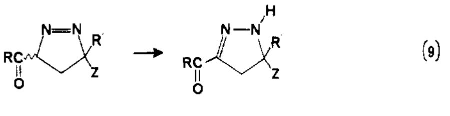
acetate and acetonitrile was formed in 30% yield under similar conditions. The potential suitability of $Rh_6(CO)_{16}$ for catalytic oxazole formation is evident in this result, but this line of investigation was not pursued further.[24]

Most striking of the results reported in Table IV is the production of a disproportionate amount of diethyl glutaconate when the reaction between ethyl diazoacetate and ethyl acrylate is performed in the presence of $V(CO)_6$. The results obtained were reproducible, but a similar activity for the formation of **2** was not observed from reactions with methacrylonitrile or between α-diazoacetophenone and ethyl acrylate. The metal-centered radical species $V(CO)_6$[25] is unique among the mononuclear metal carbonyls employed in this investigation, and additional effort is required to identify its role in the production of diethyl glutaconate.

Discussion

The results obtained for molybdenum-promoted reactions of diazocarbonyl compounds with α,β-unsaturated esters and nitriles clearly suggest that cyclopropane formation and the concurrent production of vinyl CH insertion products are the direct result of the production of 1-pyrazoline intermediates (Scheme I). Neither $Mo(CO)_6$ nor $Mo_2(OAc)_4$ influence the rates for dipolar addition of the diazocarbonyl compound to the olefin, and neither affects the decomposition rates, product yields, or product distributions resulting from thermal decomposition of representative 1-pyrazolines. Relatively minor rate acceleration is observed for ethyl diazoacetate decomposition performed in the presence of these molybdenum compounds (Table III), particularly in reactions with the less reactive methyl methacrylate and methacrylonitrile, but decreased cyclopropane formation accompanies these rate increases (Figures 2 and 3). However, although 1-pyrazoline formation and its subsequent decomposition are unaffected by $Mo(CO)_6$ or $Mo_2(OAc)_4$, these promoters are essential for effective formation of **1** and **2**. In the absence of these promoters, 2-pyrazoline products dominate.

The effectiveness of $Mo(CO)_6$ and $Mo_2(OAc)_4$ appears to be associated with their ability to prevent tautomerization of the initially formed 1-pyrazoline (eq 9) and to



be intimately linked with their facility for competitive decomposition of the reactant diazocarbonyl compound. The use of weak bases such as pyridine and triphenylphosphine, even in quantities comparable to those of the molybdenum promoters, facilitates tautomerization and suggests that 2-pyrazoline formation is autocatalytic. Entrapment by molybdenum compounds of the basic 2-pyrazoline would therefore promote the alternate dinitrogen extrusion pathway for 1-pyrazoline decomposition. Indeed, when 2-pyrazoline was generated by the addition of a catalytic amount of pyridine to ethyl diazoacetate in methacrylonitrile containing either $Mo(CO)_6$ or $Mo_2(OAc)_4$, the yield ratio of cyclopropane to 2-pyrazoline paralleled the molar ratio of molybdenum promoter to initial 2-pyrazoline (pyridine). In separate investigations 1-pyrazolines were not observed to form stable coordination complexes with $Mo_2(OAc)_4$.

Dipolar addition reactions of diazo compounds with alkenes have been studied in considerable detail, and convincing evidence has been presented that these reactions are HO(diazo compound)–LU(dipolarophile) controlled.[26-28] As is reinforced by results obtained in this study (Table III), these reactions are subject to electronic influences that markedly affect rates for cycloaddition.[2,29,30] Although dipolar addition is unaffected by the presence of molybdenum promoters, subtle changes in the rates for dipolar addition influence the outcome of molybdenum promoted reactions. Two decomposition pathways for diazocarbonyl compounds are evident: (1) dipolar addition and (2) molybdenum-catalyzed decomposition, whose reaction products include carbenoid dimers and, as described in Figure 1, the dihydro reduction product derived from the diazo reactant. With the reactive ethyl acrylate or acrylonitrile/diazocarbonyl compound combination, dipolar addition is dominant, and because of the correspondingly rapid tautomerization of the addition-derived 1-pyrazoline, increasing the relative concentration of molybdenum promoters actually leads to an increased yield of dinitrogen extrusion products **1** and **2**. In contrast, methyl methacrylate and methacrylonitrile undergo dipolar addition at recognizably slower rates that are competitive with those for molybdenum-catalyzed decomposition of the reactant diazocarbonyl compound. Consequently, increasing the relative concentration of molybdenum promoters leads to increased rates for decomposition of the diazocarbonyl compound (Figure 2) and decreased yields of **1** and **2** (Figures 1 and 3). The effects of reaction solvents on products derived from these molybdenum-promoted reactions can also be identified with the influence of these solvents on the rates for cycloaddition.[31]

Thermal decomposition of 1-pyrazolines that are not subject to rapid tautomerization has been investigated in detail and, although the mechanism of this reaction is subject to several interpretations,[32,33] the formation of derivative cyclopropane and olefin products is generally observed.[6,34] Although dinitrogen extrusion is usually considered to require thermal activation, a limited number of examples have recently appeared that suggest that substituent-derived electronic influences on 1-pyrazoline decomposition can result in a lower energy of activation for dinitrogen extrusion than for dipolar addition.[35-38] If,

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(24) The use of palladium(II) acetate[13] and copper(II) triflate[14] for oxazole formation from ethyl diazoacetate has been reported.

(25) Pratt, D. W.; Myers, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 6470.

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(33) Begley, M. J.; Dean, F. M.; Houghton, L. E.; Johnson, R. S.; Park, K. B. *J. Chem. Soc., Chem. Commun.* **1978**, 461.

(34) Bergman, R. G. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1.

indeed, 1-pyrazolines derived from dipolar addition undergo decomposition at faster rates than those for their formation, as appears to be evident with the systems examined in this study, then the absence of pyrazoline products cannot be taken, as is often the case, as evidence for carbenoid involvement in cyclopropane formation and vinyl CH insertion. Furthermore, since electron-withdrawing substituents, such as the benzoyl or carboalkoxy groups that are bound to the diazo carbon, facilitate dinitrogen extrusion, the presence of these substituents can be expected to promote the dipolar addition/1-pyrazoline decomposition pathway for cyclopropane formation even in the presence of transition-metal compounds that normally catalyze olefin cyclopropanation. The advantage of transition-metal catalysts for cyclopropane formation in reactions between diazo compounds and α,β-unsaturated carbonyl compounds or nitriles may only be due to the inhibition of 1-pyrazoline tautomerization. As indicated by results obtained for 1-pyrazoline decomposition in this investigation, dinitrogen extrusion from activated 1-pyrazolines that do not tautomerize does not require the intervention of transition-metal promoters. In addition, the production of alkenes designated as formal vinyl CH insertion products, rather than suggesting the involvement of carbenoid intermediates in transition-metal-catalyzed reactions,[39] is indicative of 1-pyrazoline involvement or, in select cases, of thermal[40] or catalytic[41] isomerization of cyclopropane products.

Paulissen has recently suggested that $Fe(CO)_5$ catalyzes the dipolar addition of ethyl diazoacetate to norbornadiene since cycloreversion of presumed intermediate pyrazolines, which results in the production of 3-carboethoxypyrazole and cyclopentadiene, is not observed in its absence.[42] This interpretation is inconsistent with the role of $Fe(CO)_5$ that is suggested in this investigation. An alternate interpretation, that dipolar addition is independent of $Fe(CO)_5$, but that $Fe(CO)_5$ prevents tautomerization of the initially formed 1-pyrazoline, appears more likely. Although there is no direct analogy, cycloreversion of the 1-pyrazoline[43,44] may be more favorable energetically than cycloreversion of the derivative 2-pyrazoline,[45] but additional details of this novel transformation are required before a definitive conclusion can be reached.

In $Mo(CO)_6$-promoted reactions of diazocarbonyl compounds with α,β-unsaturated esters and nitriles the coordinatively unsaturated $Mo(CO)_5$ appears to be the active intermediate responsible for the direction that these reactions follow. Carbon monoxide inhibits the production of **1** and **2** (Table II) and triphenylphosphine, which is the more labile ligand in $Mo(CO)_4(Ph_3P)_2$, causes enhanced production of the 2-pyrazoline product. The relative capability of the carbonyl complexes of elements in the chromium triad to direct cyclopropane formation, $Mo(CO)_6 > Cr(CO)_6 > W(CO)_6$,[16] which parallels their relative ease for displacement of a carbonyl ligand,[46] is consistent with this interpretation. However, carbonyl displacement through a second-order nucleophilic process[47] may also account for the observed activities of the molybdenum carbonyl promoters. Organic nitriles and unsaturated carbonyl compounds can be assumed to compete with diazo compounds for association with molybdenum carbonyls[48,49] and thereby explain the relative inactivity of $Mo(CO)_6$ toward decomposition of ethyl diazoacetate (Figure 2).

The use of $Mo(CO)_6$ for a broad selection of chemical transformations has been described recently.[50] Alternative promoters such as $Mo_2(OAc)_4$, Cp_2ZrCl_2, and $V(CO)_6$, whose parallel activities have been identified in this investigation (Table IV), have not been widely employed. Their similar activity for 2-pyrazoline entrapment suggests a specificity that has not been realized with Lewis acids in similar transformations[51] and indicates that they may be at least as active as $Mo(CO)_6$ in rearrangement reactions of strained ring heterocyclic systems.[21,52]

Experimental Section

Materials and Methods. Proton magnetic resonance spectra were obtained with the Varian FT-80A spectrometer; chemical shifts are reported in δ units, using tetramethylsilane as the internal standard. Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 2720 gas chromatograph with thermal conductivity detectors. Mass spectra were taken on a Finnigan Model 1015 GC/mass spectrometer operated at 70 eV, and IR spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer. Molybdenum hexacarbonyl was obtained from Alfa, and $Mo_2(OAc)_4$ was prepared from $Mo(CO)_6$ by treatment with acetic acid in diglyme.[53] Derivative molybdenum complexes $Mo(CO)_4(Ph_3P)_2$,[54] $Mo(CO)_4(pip)_2$,[55] $Mo(CO)_4(Ph_3P)(pip)$,[56] and $Mo(N_2)_2(dppe)_2$[57] were prepared and characterized by literature procedures. Transition-metal compounds reported in Table IV were obtained commercially and used without further purification. α-Diazoacetophenone was prepared from benzoyl chloride and diazomethane.[1]

Reactions of Diazocarbonyl Compounds with α,β-Unsaturated Carbonyl and Nitrile Systems in the Presence of Molybdenum Promoters. The diazocarbonyl compound (2.0 mmol) in 2 mL of the unsaturated component was added to a stirred solution of molybdenum hexacarbonyl or molybdenum(II) acetate in 3 mL of the α,β-unsaturated nitrile or carbonyl compound at 65 °C. The progress of these reactions was followed by measuring gas evolution in a closed system. Reactions promoted by $Mo_2(OAc)_4$ were performed under nitrogen. Following complete gas evolution the olefinic solvent was evaporated. Ether was then added and the resulting solution was washed twice with water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure to remove solvent.

Quantitative analyses were obtained with the use of an internal standard, dibenzyl ether, which was added to the reaction mixture

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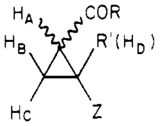
Table V. NMR Spectral Data for Cyclopropane Derivatives[a]



				chemical shift, δ [b]				coupling constant, Hz[c]					
R	R'	Z	isomer	H_A	H_B	H_C	R'(H_D)	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
C_6H_5[d]	H	COOEt[e]	*E*	3.18	1.8-1.4		2.39	6.2	8.1	3.9	4.0	6.8	7.7
			Z	2.78	1.90	1.35	2.28	6.7	8.3	9.3	4.7	6.4	8.3
C_6H_5[d]	CH_3	COOMe[f]	*E*	3.29	1.68	1.62	1.27 (s)	6.7	8.2		4.0		
			Z	2.56	2.12	1.22	1.56 (s)	6.6	8.2		4.6		
C_6H_5[d]	H	CN	*E*	3.27	1.8-1.5		2.16	6.5	8.2	4.4	4.7	6.8	7.6
			Z	3.14	1.8-1.4		2.06	6.3	8.2	9.1	4.4	6.5	7.8
C_6H_5[d]	CH_3	CN	*E*	3.24	1.78	1.67	1.35 (s)	6.8	8.5		5.1		
			Z	2.88	2.14	1.34	1.63 (s)	6.4	7.9		5.0		
C_6H_5[d]	H	$COCH_3$[g]	*E*	3.23	1.8-1.4		2.70	6.0	8.3	3.8	5.0	6.2	8.0
			Z	2.90	1.95	1.38	2.47	6.6	8.2	9.3	4.5	6.7	8.2
EtO[h]	H	COOEt[h]	*E*	2.20	1.6-1.3		2.20	6.8	8.6		[o]	6.8	8.6
			Z	2.04	1.67	1.20	2.04	6.1	8.1		4.6	8.1	6.1
EtO[i]	CH_3	COOMe[j]	*E*	2.36	1.61	1.36	1.41 (s)	6.6	8.6		4.1		
			Z	1.86	1.86	1.06	1.51 (s)	6.2	8.2		4.4		
EtO[k]	H	CN	*E*	2.26	1.7-1.4		1.95	6.2	8.3	4.5	5.0	7.3	8.0
			Z	2.13		1.9-1.3		5.9	8.0	8.4	4.6	[o]	[o]
EtO[l]	CH_3	CN	*E*	2.31	1.60	1.39	1.49 (s)	7.0	8.7		5.2		
			Z	1.86	1.33	1.18	1.49 (s)	6.4	8.4		5.2		
EtO[m]	H	$COCH_3$[n]	*E*	2.18	1.5-1.2		2.45	6.0	8.3	3.8	[o]	[o]	[o]
			Z	2.3-2.0	1.66	1.24	2.3-2.0	[o]	[o]	[o]	4.5	7.0	7.8

[a] Spectra taken at 30 °C in $CDCl_3$. [b] ±0.02 ppm. [c] ±0.1 Hz. [d] Phenyl adsorptions observed at δ 8.1-7.9 (2 H) and at 7.7-7.4 (3 H). [e] *E* isomer: δ 4.19 (q, *J* = 7.1 Hz) and 1.28 (t, *J* = 7.1 Hz); *Z* isomer: δ 3.99 (q, *J* = 7.1 Hz) and 1.05 (t, *J* = 7.1 Hz). [f] *E* isomer: δ 3.78 (s); *Z* isomer: δ 3.50 (s). [g] *E* isomer: δ 2.34 (s); *Z* isomer: δ 2.19 (s). [h] *E* isomer: δ 4.15 (q, *J* = 7.1 Hz) and 1.26 (t, *J* = 7.1 Hz); *Z* isomer: δ 4.14 (q, *J* = 7.1 Hz) and 1.25 (q, *J* = 7.1 Hz). [i] *E* isomer: δ 4.21 (q, *J* = 7.1 Hz) and 1.26 (t, *J* = 7.1 Hz); *Z* isomer: δ 4.13 (q, *J* = 7.1 Hz) and 1.25 (t, *J* = 7.1 Hz). [j] *E* isomer: δ 3.72 (s); *Z* isomer: δ 3.67 (s). [k] *E* isomer: δ 4.19 (q, *J* = 7.1 Hz) and 1.29 (t, *J* = 7.1 Hz); *Z* isomer: δ 4.26 (q, *J* = 7.1 Hz) and 1.31 (t, *J* = 7.1 Hz). [l] *E* isomer: δ 4.20 (q, *J* = 7.1 Hz) and 1.29 (t, *J* = 7.1 Hz); *Z* isomer: δ 4.24 (q, *J* = 7.1 Hz) and 1.21 (t, *J* = 7.1 Hz). [m] *E* isomer: δ 4.14 (q, *J* = 7.1 Hz) and 1.27 (t, *J* = 7.1 Hz); *Z* isomer: δ 4.12 (q, *J* = 7.1 Hz) and 1.24 (t, *J* = 7.1 Hz). [n] *E* isomer: δ 2.30 (s); *Z* isomer: 2.26 (s). [o] Not determined.

prior to extraction. Product yields were determined by GC and ^{1}H NMR analyses, and comparative results for cyclopropane and vinyl CH insertion product yields, isomer ratios, and the presence of carbenoid dimers demonstrated the validity of the analytical method. The 2-pyrazoline products could not be analyzed directly by GC because of their thermal instability and, consequently, their yields were determined by NMR analyses. Yields from GC analyses were calculated with the use of previously determined thermal conductivity values. Isomer separations were conveniently obtained with base line resolution on 10% DEGS or OV-275 columns. In all cases the *E* cyclopropane isomer eluted prior to the *Z* isomer, and vinyl CH insertion products were generally observed to elute after the *Z* cyclopropane isomer.

The individual cyclopropane geometrical isomers were separated by GC methods and their structures were determined by ^{1}H NMR analyses (Table V). The cis and trans geometries of cyclopropane isomers derived from ethyl acrylate, acrylonitrile, and methyl vinyl ketone were readily apparent from their characteristic H_AH_D coupling constants.[58] Isomeric cyclopropanes derived from methyl methacrylate and methacrylonitrile were assigned by chemical shift comparisons with analogous derivatives reported in Table V and with model cyclopropane derivatives.[59] The relative effect of C_6D_6 on the chemical shift of isomeric cyclopropanes further confirmed the assigned stereochemistry,[60,61] e.g., for R = OEt, R' = CH_3, Z = COOMe (compare with chemical shifts in Table V): *E* isomer, NMR δ 2.48 (H_A), 1.25 (H_B), 1.44 (H_C), 1.50 (CH_3), 3.20 (OMe), 3.91 (OCH_2), 0.91 (CH_3); *Z* isomer, NMR δ 1.90 (H_A), 1.52 (H_B), 0.56 (H_C), 1.07 (CH_3), 3.40 (OMe), 3.95 (OCH_2), 0.95 (CH_3). Mass spectral analyses provided the identity of the molecular ions for cyclopropane derivatives. Vinyl CH insertion products **2** were also collected and identified by NMR analyses (Table VI).

Reactions of Diazocarbonyl Compounds with α,β-Unsaturated Esters and Nitriles in the Presence of Pyridine. The diazocarbonyl compound (2.0 mmol) in 2 mL of the unsaturated component was added to a stirred solution of pyridine (5-50 mol %) in 3 mL of the unsaturated ester or nitrile at 65 °C. After 2 h the solvent was evaporated under reduced pressure to yield the corresponding 2-pyrazolines in 90-100% yield. Pertinent NMR data for these derivatives is presented in Table VI.[62]

In the absence of pyridine or in the presence of <2% $Mo(CO)_6$, ethyl diazoacetate reacted with ethyl acrylate to form a mixture of 1- and 2-pyrazolines. The 1-pyrazoline structure was suggested in NMR analyses of these reaction mixtures: NMR ($CDCl_3$) δ 5.48 (t, *J* = 7 Hz, CHCOOEt) and 2.13 (t, *J* = 7 Hz, CH_2) for the trans isomer and δ 5.14 (t, *J* = 9 Hz, CHCOOEt) and 2.15 (t, *J* = 9 Hz, CH_2) for the cis isomer. At 25 °C in the absence of promoter the trans/cis 1-pyrazoline ratio was 3.5; at 52 °C the observed ratio was 2.0. The *cis*-1-pyrazoline was observed to decompose at a faster rate than the trans isomer, but the details of this decomposition were not pursued.

Kinetic Evaluation of Reactions between Ethyl Diazoacetate and α,β-Unsaturated Esters and Nitriles. Reaction solutions were prepared by the combination of olefin, ethyl diazoacetate, promoter, and internal standard (*p*-chlorotoluene) in a 10-mL volumetric flask. Benzene was added with thorough mixing to raise the total volume of the homogeneous reaction solution to 10.0 mL. The initial concentrations of reactants in these solutions are reported in Table III. Reaction solutions were heated at the appropriate temperature (±1 °C), and 0.50-mL aliquots were removed at regular time intervals and immediately injected into 0.50 mL of a ethanolic solution containing 10% (v/v)

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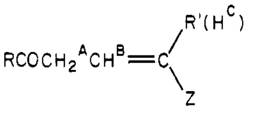
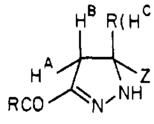
[62] The detailed characterization of these pyrazolines and their thermal reactions will be presented in a forthcoming publication.

Table VI. NMR Spectral Data for 2 and 3[a]



2



3b

R	R'	Z	2, chemical shift, ppm[b]			3, chemical shift, ppm[c]		
			H^A	H^B	$R'(H^C)$	H^A	H^B	$R'(H^C)$
C_6H_5	H	COOEt	3.95	7.10	5.90	3.43	3.33	4.35
C_6H_5	CH_3	COOMe	4.30	6.48	1.92			
C_6H_5	H	CN	3.88	6.98	5.97	3.46	3.29	4.65
C_6H_5	CH_3	CN	3.88	6.50	1.86	3.65	3.15	1.67
C_6H_5	H	$COCH_3$	3.88	7.03	6.13			
EtO	H	COOEt	3.22	7.04	5.92	3.26	3.14	4.50
EtO	CH_3	COOMe	2.79	7.14	1.68	3.50	3.18	1.52
EtO	H	CN	3.34	6.73	5.98	3.24	3.13	4.55
EtO	H	CN				(3.32)	(3.20)	(4.75)
EtO	CH_3	CN	3.20	6.65	1.58	3.45	2.96	1.63
EtO	H	$COOCH_3$	2.80	7.03	5.87			

[a] Spectra taken at 30 °C in $CDCl_3$. Chemical shifts are reported with precision of ±0.02 ppm. [b] Data are given for the *E* isomer only; coupling constants (J_{trans} = 15-17 Hz, J_{AB} = 6.5-7.5 Hz, and J_{AC} = 1-2 Hz) are consistent with the structural assignments. The corresponding *Z* isomers were also observed but generally as the minor component of the olefin fraction ($E/Z > 3$). [c] With the exception of cycloaddition of ethyl diazoacetate to acrylonitrile, only **3b** was observed. Geminal coupling constants for **3b** (R' = CH_3) were 16-18 Hz; those for **3** (R' = H) were not perceptible and, consequently, chemical shift data are reported for the internal H_AH_B absorptions of the ABC system. The chemical shift of the NH proton is observed in the region δ 7.5-6.5.

of concentrated hydrochloric acid. This quenching procedure caused the immediate and quantitative conversion of unreacted ethyl diazoacetate to ethyl chloroacetate. Ether (5 mL) and water (2 mL) were added to the acidic solution, the resulting mixture was thoroughly shaken with a vortex mixer, and the aqueous layer was removed. The resulting ether solution was washed with 2 mL of saturated sodium bicarbonate in a similar manner and then dried over anhydrous mangesium sulfate. The sample was subjected to direct GC analysis on a 10% Carbowax 20 M column, and the peak areas of ethyl chloroacetate and *p*-chlorotoluene were determined. Kinetic determinations were obtained with a minimum of 10 aliquots, and rate constants were calculated from the slope of a plot of ln (A_0/A) vs. time, where *A* is the area ratio of ethyl chloroacetate to standard. Duplicate runs were obtained for each kinetic determination. Pseudo-first-order kinetics were observed through 2 half-lives. Reactions performed at different concentrations of the α,β-unsaturated component demonstrated first-order rate dependence on the olefinic substrate.

For representative kinetic determinations in each series, the progress of reaction was followed by measuring the rate of cyclopropane formation as well as the rate for ethyl diazoacetate consumption. Without exception rate constants for cyclopropane formation were identical with rate constants for ethyl diazoacetate decomposition. Furthermore, the ratio of cyclopropane isomers remained constant throughout the reaction.

Activation parameters were calculated from a plot of ln (k/T) vs. ($1/T$), using a minimum of three kinetic rate constants obtained over the following temperature ranges: 37–60 °C for ethyl acrylate, 52–85 °C for methyl methacrylate, 42–74 °C for acrylonitrile, and 52–85 °C for methacrylonitrile. Correlation coefficients of greater than 0.98 characterized these determinations.

Decomposition of 1-Pyrazolines. Diethyl diazomalonate[63] was unreactive with methacrylonitrile at 60 °C even after 48 h and at 90 °C had proceeded to only 10% decomposition after 24 h. Analysis of the reaction solution at this time indicated a complex mixture of which diethyl 2-cyano-2-methyl-1,1-cyclopropanedicarboxylate was the only major product derived from the diazomalonate reactant: NMR ($CDCl_3$) δ 4.28 (q, *J* = 7.1 Hz, CH_2O), 4.25 (q, *J* = 7.1 Hz, CH_2O), 2.03 (d, J_{gem} = 5.2 Hz, 1 H), 1.63 (d, J_{gem} = 5.2 Hz, 1 H), 1.51 (s, CH_3), 1.33 (t, *J* = 7.1 Hz, 6 H); mass spectrum, *m/e* (relative intensity) 225 (4.5, M^+), 199 (35, M – CN), 180 (50, M – OEt), 169 (75), 152 (51), 151 (81), 142 (47), 134 (95), 133 (95), 130 (96), 129 (60), 128 (44), 127 (99), 125 (50), 124 (48), 120 (48), 115 (56), 107 (77), 105 (62), 99 (89).

Ethyl diazopropionate[64] was added to methacrylonitrile at 25 °C in the presence and absence of molybdenum promoters. In a representative procedure, 64 mg of ethyl diazopropionate (0.50 mmol) was added to 0.34 g of methacrylonitrile (5.0 mmol) and reaction was allowed to proceed at 25 °C for 48 h. Distillation of excess methacrylonitrile under reduced pressure resulted in a yellow residue. The 1-pyrazoline intermediate (**5**; Y = COOEt, R = CH_3, Z = CN), presumed to be the *E* isomer, was evident from NMR absorptions centered at δ 2.72 and 2.04 (d, *J* = 13 Hz), but derivative cyclopropane products (E/Z = 0.8) were observed even within 5 min after addition of the diazo compound to methacrylonitrile. The initially formed cyclopropane products were assumed to arise from rapid decomposition of the 1-pyrazoline *Z* isomer. Slow decomposition of the 1-pyrazoline *E* isomer occurred at 25 °C with an estimated half-life of 2 days, and no difference was observed for the rate of decomposition in the presence or absence of molybdenum promoters. Cyclopropane products were identified from their characteristic spectra. Ethyl 2-cyano-1,2-dimethylcyclopropanecarboxylate: *E* isomer, NMR ($CDCl_3$) δ 4.18 (q, *J* = 7.1 Hz, CH_2O), 1.7–1.5 (m, 2 H), 1.55 (s, 3 H), 1.42 (s, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H); *Z* isomer, NMR ($CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, CH_2O), 2.12 (d, J_{gem} = 5.0 Hz, 1 H), 1.47 (s, 3 H), 1.36 (s, 3 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 0.88 (d, J_{gem} = 5.0 Hz, 1 H). Products from vinyl CH insertion were not observed from reactions performed at 25 °C, and the cyclopropane products generally accounted for greater than 80% of the recovered products.

Phenyldiazomethane[65] (0.67 g, 5.7 mmol) in 15 mL of anhydrous ether was combined with 5.7 g of methyl methacrylate. After 22 h at 0 °C under a nitrogen atmosphere, ether and excess methyl methacrylate were distilled under reduced pressure to yield a pale-yellow oil, which contained approximately equal amounts of the two isomeric 1-pyrazolines in greater than 85% purity with cyclopropane products as the sole contaminants. **5** (Y = Ph, R = H, Z = COOMe): *Z* isomer, NMR ($CDCl_3$) δ 5.58 (t, *J* = 8 Hz, CHPh), 3.76 (s, OCH_3), 2.10 (d of d, *J* = 14, 8 Hz, 1 H), 1.85 (d of d, *J* = 14, 8 Hz), 1.81 (s, CH_3); *E* isomer, NMR ($CDCl_3$) δ 5.46 (t, 10 Hz, CHPh), 3.83 (s, OCH_3), 2.61 (d of d, *J* = 14 Hz, 10 Hz, 1 H), 1.53 (s, CH_3), 1.22 (d of d, *J* = 14, 10 Hz, 1 H). Slow decomposition of these cycloaddition products occurred at 25 °C

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with an estimated half-life of 1 day, and both isomers were observed to undergo decomposition at approximately equal rates. Neither $Mo(CO)_6$ nor $Mo_2(OAc)_4$, even when employed in equivalent amounts relative to the 1-pyrazoline reactant, markedly affected the rate of decomposition, cyclopropane yield, or cyclopropane isomer ratio. The two isomeric methyl 1-methyl-2-phenylcyclopropanecarboxylates[66] were the sole products from pyrazoline decomposition: *Z* isomer, NMR ($CDCl_3$) δ 7.45–7.25 (m, 5 H), 3.28 (s, OCH_3), 2.33 (d of d, J = 7.3, 8.6 Hz, CHPh), 1.92 (d of d, J = 4.8, 7.3 Hz, 1 H), 1.48 (s, CH_3), 1.10 (d of d, J = 4.8, 8.6 Hz, 1 H); *E* isomer, NMR ($CDCl_3$) δ 7.50–7.25 (m, 5 H), 3.71 (s, OCH_3), 2.79 (d of d, J = 7.1, 9.1 Hz, CHPh), 1.67 (d of d, J = 4.6, 9.1 Hz, 1 H), 1.14 (d of d, J = 4.6, 7.1 Hz, 1 H), 0.96 (s, CH_3). The *Z* isomer was observed to elute first from a Carbowax 20M GC column and was the major product from pyrazoline decomposition (Z/E = 2.0).

3-Methyl-3-(carbomethoxy)-1-pyrazoline (**7**) was prepared from methyl methacrylate by treatment with diazomethane.[67] Thermal decomposition of **7** in the presence or absence of molybdenum promoters in sealed tubes at 90 °C and at 155 °C for 20 h produced mixtures of cyclopropane and olefinic products whose composition corresponded to that previously reported for the pyrolysis of **7**.[22] For reactions performed at 155 °C, methyl 1-methylcyclopropanecarboxylate was produced in 68% yield (67% at 127 °C and 62% at 90 °C), and the olefinic products, *Z* and *E* isomers of methyl 2-methyl-2-butenoate and methyl 2-methyl-3-butenoate, were formed in 11%, 18%, and 4%, respectively (12%, 16%, and 5%, respectively, at 127 °C and 13%, 20%, and 5% at 90 °C). Reactions performed in the presence of either $Mo(CO)_6$ or $Mo_2(OAc)_4$ gave identical results.

Reactions of Ethyl Diazoacetate with α,β-Unsaturated Esters and Nitriles in the Presence of Transition-Metal Compounds. In a typical procedure a measured amount of the transition-metal compound (0.023 mmol) was transferred to a round-bottom flask fitted with a reflux condenser followed by the α,β-unsaturated substrate (46 mmol) and ethyl diazoacetate (2.3 mmol). All operations were performed under nitrogen. Benzene (50% v/v α,β-unsaturated substrate) was generally employed for reactions performed in the presence of metal carbonyls. Reaction solutions were heated at 65 °C under nitrogen for 24 h and then cooled. Internal standard (dibenzyl ether) and 125 mL of ethyl ether were added, and the resulting solution was washed twice with 10% aqueous hydrochloric acid and once with saturated sodium bicarbonate solution. The ether solution was dried over anhydrous magnesium sulfate, and the solvent was distilled under reduced pressure. The acid wash did not remove 2-pyrazoline products. Analyses were performed as previously described.

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Registry No. (*E*)-**1** (R = C_6H_5; R′ = H; Z = COOEt), 1518-20-3; (*Z*)-**1** (R = C_6H_5; R′ = H; Z = COOEt), 15982-18-0; (*E*)-**1** (R = EtO; R′ = H; Z = COOEt), 3999-55-1; (*Z*)-**1** (R = EtO; R′ = H; Z = COOEt), 710-43-0; (*E*)-**1** (R = C_6H_5; R′ = CH_3; Z = COOMe), 15732-78-2; (*Z*)-**1** (R = C_6H_5; R′ = CH_3; Z = COOMe), 82706-80-7; (*E*)-**1** (R = EtO; R′ = CH_3; Z = COOMe), 13950-03-3; (*Z*)-**1** (R = EtO; R′ = CH_3; Z = COOMe), 13950-18-0; (*E*)-**1** (R = C_6H_5; R′ = H; Z = CN), 64390-09-6; (*Z*)-**1** (R = C_6H_5; R′ = H; Z = CN), 64390-08-5; (*E*)-**1** (R = EtO; R′ = H; Z = CN), 3999-56-2; (*Z*)-**1** (R = EtO; R′ = H; Z = CN), 699-23-0; (*E*)-**1** (R = C_6H_5; R′ = CH_3; Z = CN), 73178-39-9; (*Z*)-**1** (R = C_6H_5; R′ = CH_3; Z = CN), 73178-40-2; (*E*)-**1** (R = EtO; R′ = CH_3; Z = CN), 73178-41-3; (*Z*)-**1** (R = EtO; R′ = CH_3; Z = CN), 73178-42-4; (*E*)-**1** (R = C_6H_5; R′ = H; Z = $COCH_3$), 64390-04-1; (*Z*)-**1** (R = C_6H_5; R′ = H; Z = $COCH_3$), 64390-03-0; (*E*)-**1** (R = EtO; R′ = H; Z = $COCH_3$), 13949-95-6; (*Z*)-**1** (R = EtO; R′ = H; Z = $COCH_3$), 13950-15-7; (*E*)-**2** (R = C_6H_5; R′ = H; Z = COOEt), 82706-81-8; (*E*)-**2** (R = EtO; R′ = H; Z = COOEt), 73178-43-5; (*E*)-**2** (R = C_6H_5; R′ = CH_3; Z = COOMe), 82706-84-1; (*E*)-**2** (R = EtO; R′ = CH_3; Z = COOMe), 82706-85-2; (*E*)-**2** (R = C_6H_5; R′ = H; Z = CN), 82706-87-4; (*E*)-**2** (R = EtO; R′ = H; Z = CN), 81251-00-5; (*E*)-**2** (R = C_6H_5; R′ = CH_3; Z = CN), 82706-89-6; (*E*)-**2** (R = EtO; R′ = CH_3; Z = CN), 82706-90-9; (*E*)-**2** (R = C_6H_5; R′ = H; Z = $COCH_3$), 82706-91-0; (*E*)-**2** (R = EtO; R′ = H; Z = $COCH_3$), 82706-99-8; **3a** (R = EtO; R′ = H; Z = CN), 64847-17-2; **3b** (R = C_6H_5; R′ = H; Z = COOEt), 82706-82-9; **3b** (R = EtO; R′ = H; Z = COOEt), 82706-83-0; **3b** (R = EtO; R′ = CH_3; Z = COOMe), 82706-86-3; **3b** (R = C_6H_5; R′ = H; Z = CN), 82706-88-5; **3b** (R = EtO; R′ = H; Z = CN), 67872-78-0; **3b** (R = C_6H_5; R′ = CH_3; Z = CN), 82707-00-4; **3b** (R = EtO; R′ = CH_3; Z = CN), 82707-01-5; (*E*)-**5** (Y = COOEt; R = CH_3; Z = CN), 82706-93-2; (*Z*)-**5** (Y = COOEt; R = CH_3; Z = CN), 82706-94-3; (*E*)-**5** (Y = Ph; R = H; Z = COOMe), 82706-98-7; (*Z*)-**5** (Y = Ph; R = H; Z = COOMe), 82706-97-6; (*E*)-**6** (Y = COOEt; R = CH_3; Z = CN), 82706-95-4; (*Z*)-**6** (Y = COOEt; R = CH_3; Z = CN), 82706-96-5; (*E*)-**6** (Y = Ph; R = H; Z = COOMe), 27067-43-2; (*Z*)-**6** (Y = Ph; R = H; Z = COOMe), 56434-66-3; **7**, 6117-22-2; **8**, 6206-25-3; (*E*)-**9**, 6622-76-0; (*Z*)-**9**, 5953-76-4; **10**, 51747-33-2; $Mo(CO)_4(Ph_3P)_2$, 15096-70-5; $Mo(CO)_4(pip)_2$, 59967-36-1; $Mo(CO)_4(Ph_3P)(pip)$, 82768-69-2; $Mo(N_2)_2(dppe)_2$, 41700-58-7; $Mo(CO)_6$, 13939-06-5; $Mo_2(OAc)_4$, 14221-06-8; α-diazoacetophenone, 3282-32-4; ethyl diazoacetate, 623-73-4; ethyl acrylate, 140-88-5; methyl methacrylate, 80-62-6; acrylonitrile, 107-13-1; methacrylonitrile, 126-98-7; 3-buten-2-one, 78-94-4; pyridine, 110-86-1; diethyl diazomalonate, 5256-74-6; diethyl 2-cyano-2-methyl-1,1-cyclopropanedicarboxylate, 82706-92-1; ethyl diazopropionate, 6111-99-5; phenyldiazomethane, 766-91-6.

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