20574 and partial support to D.P.P. from departmental Training Grant T 32 CA 09112). We also thank Dr. C. Costello for obtaining exact mass measurements.

**Registry No. 3**, 1725-03-7; **4a**, 72037-28-6; **4b**, 73177-52-3; **4c**, 73192-74-2; **4d**, 73177-53-4; **4e**, 73177-54-5; **4f**, 73177-55-6; **5a**, 73177-56-7; **5b**, 73177-57-8; **5c**, 73177-58-9; **5d**, 73177-59-0; **5e**, 73177-60-3; **5f**, 73177-61-4; **6a**, 72037-29-7; **6b**, 73177-62-5; **6c**, 73177-63-6; **6d**, 73177-64-7; **6e**, 73177-65-8.

**Supplementary Material Available:** Figure 1, a photograph of a CPK model of templated, preclosure intermediate 1 (1 page). Ordering information is given on any current masthead page.

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## Molybdenum Hexacarbonyl Catalyzed Cyclopropanation of α,β-Unsaturated Esters and Nitriles with Diazocarbonyl Compounds

*Summary:* Molybdenum hexacarbonyl, when employed in catalytic amounts, effectively promotes cyclopropanation of acrylonitrile, methacrylonitrile, and ethyl acrylate by ethyl diazoacetate and α-diazoacetophenone; the intermediacy of molybdenum carbene species in the formation of cyclopropane derivatives is suggested.

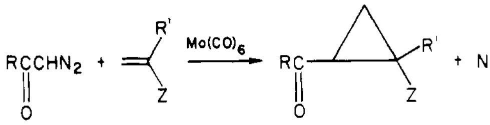
*Sir:* The cyclopropanation of unsaturated compounds by methylene and methine synthons has been a subject of intense interest, and numerous methodologies have been developed for this addition transformation.[1] Metal-catalyzed addition processes between diazo compounds and unsaturated substrates that occur with the loss of nitrogen are well-known in select cases for their synthetic versatility in forming cyclopropane derivatives.[2] Although metal–carbene intermediates are often proposed for these transformations[2,3] and considerable efforts have been expended to define and elucidate the reactions of diazo compounds and transition metal–carbene complexes,[4] there have been few reports of effective metal-catalyzed cyclopropanation reactions by diazo compounds[5] other than those with copper complexes.[2]

Table I. Yields of Cyclopropane Derivatives from Molybdenum Hexacarbonyl Catalyzed Reactions of Diazocarbonyl Compounds with α,β-Unsaturated Esters and Nitriles[a]

| unsatd compd | diazocarbonyl compd | *T*, °C | reacn time, h | % yield of 1[b] | %*E*/%*Z*[c] |
|---|---|---|---|---|---|
| $H_2C{=}CHCN$ | $C_6H_5COCHN_2$ | 65 | 7 | 77 | 2.2 |
| | | 25 | 70 | 63 | 2.2 |
| | $EtOOCCHN_2$ | 65 | 7 | 46 | 1.1 |
| | | 25 | 72 | 46 | 1.4 |
| $H_2C{=}C(CH_3)CN$ | $C_6H_5COCHN_2$ | 65 | 7 | 25 | 0.93 |
| | | 25 | 72 | 19 | 1.2 |
| | $EtOOCCHN_2$ | 65 | 3 | 79 | 0.70 |
| | | 25 | 72 | 77 | 0.70 |
| $H_2C{=}CHCOOEt$ | $C_6H_5COCHN_2$ | 65 | 8 | 72 | 1.7 |
| | | 25 | 70 | 48 | 1.3 |
| | $EtOOCCHN_2$ | 65 | 8 | 31 | 1.6 |
| | | 25 | 72 | 36 | 1.5 |

[a] The diazocarbonyl compound (2.0 mmol) in 5 mL of the unsaturated compound is added to a stirred solution of molybdenum hexacarbonyl (0.30 mmol) in 10 mL of the α,β-unsaturated nitrile or ester at the appropriate reaction temperature. Progress of these reactions is followed by measuring the volume of gas that is evolved. Following complete gas evolution (generally 2 mmol), hexane is added to precipitate the molybdenum-containing products (mainly molybdenum hexacarbonyl), the solution is filtered, and the solvent is distilled. [b] Product yields were determined by GC and $^1H$ NMR analysis; the individual geometrical isomers were characterized from their singular spectral and physical properties. [c] Isomer separations were conveniently obtained by GC analyses with base line resolution on a 10% DEGS or OV-275 column. The variability in the yields of individual isomers was less than ±2%.

Consideration of the facility with which molybdenum binds dinitrogen[6] and the relative high reactivity of molybdenum–carbene complexes[7] has led us to investigate the reactions of diazo compounds with molybdenum(0). Diazoalkane complexes of molybdenum have recently been prepared[8] and (phenylmethoxycarbene)pentacarbonyl complexes of chromium, molybdenum, and tungsten have been reported to undergo cyclopropanation of α,β-unsaturated carboxylate esters,[9] albeit at elevated temperatures and in relatively low yields. We have found that molybdenum hexacarbonyl, when employed in catalytic amounts, effectively promotes cyclopropanation of conjugated esters and nitriles by diazocarbonyl compounds (eq 1). In the



(1)

1

absence of molybdenum hexacarbonyl, 1-pyrazolines are formed by 1,3-dipolar addition;[10] rapid isomerization of the initially formed addition product yields the observed 2-pyrazolines,[11] and cyclopropane formation is insignificant under reaction conditions identical with those employed in $Mo(CO)_6$-catalyzed reactions. Representative yields of

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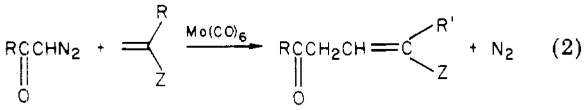
cyclopropane derivatives (1) formed from α-diazoacetophenone and ethyl diazoacetate with only 0.15 molar equiv of molybdenum hexacarbonyl are reported in Table I together with the isomeric ratios of these products.[12]

Surprisingly, cyclopropanation is generally equally effective at 25 as at 65 °C, although reaction times are significantly greater at the lower temperature. In contrast, the syntheses of cyclopropane derivatives from α,β-unsaturated esters with (phenylmethoxycarbene)pentacarbonyl complexes of chromium, molybdenum, and tungsten have been performed at 90–140 °C.[9] As has been previously observed in reactions involving carbene ligand transfer,[9] isomeric product ratios in the $Mo(CO)_6$-catalyzed cyclopropanation reactions are relatively insensitive to changes in the reaction temperature (Table I).

Although cyclopropanation is the dominant pathway for the molybdenum hexacarbonyl catalyzed reactions of diazocarbonyl compounds with unsaturated esters and nitriles, a β-vinyl C–H insertion process (eq 2) is also evident. For example, diethyl glutaconate is formed from ethyl diazoacetate and ethyl acrylate in 17% yield at 65 °C (%E/%Z = 5) and in 21% yield at 25 °C (%E/%Z > 10). Similarly, 4-benzoyl-2-methyl-2-butenenitrile is obtained from $Mo(CO)_6$-catalyzed reactions of α-diazoacetophenone with methacrylonitrile in 4% yield at 65 °C and in 2% yield at 25 °C. The yields of vinyl carbon–hydrogen insertion products are generally greater in reactions with ethyl diazoacetate than in reactions with α-diazoacetophenone. Carbon–hydrogen insertion products have been identified from copper salt catalyzed reactions of diazo esters with alkenes[13] but, as in the $Mo(CO)_6$-catalyzed reactions,[14] the mechanistic origin of this process remains speculative.[15]



$$RC(=O)CHN_2 + CH_2{=}C(R)Z \xrightarrow{Mo(CO)_6} RC(=O)CH_2CH{=}C(R')Z + N_2 \qquad (2)$$

Carbene dimers, diethyl fumarate and diethyl maleate from ethyl diazoacetate and dibenzoylethylene from α-diazoacetophenone, are also formed in these reactions. In the absence of excess conjugated ester or nitrile, these products predominate. Although we do not have direct evidence for the intermediacy of molybdenum–carbene species, the formation of carbene dimers together with the production of cyclopropanes and the relative insensitivity of the isomeric cyclopropane product ratios to changes in the reaction temperature are certainly suggestive that such intermediates are involved in these reactions. Efforts are under way to further define the mechanistic and synthetic operations of metal carbonyl catalyzed reactions of organic dinitrogen compounds.

Chromium hexacarbonyl also exhibits catalytic activity in cyclopropanation reactions, but cyclopropane formation occurs at a noticeably slower rate than in reactions involving $Mo(CO)_6$ catalysis. For example, ethyl 2-benzoyl-1-cyclopropanecarboxylate is formed in 55% yield (%E/%Z = 1.9) from the $Cr(CO)_6$-catalyzed decomposition of α-diazoacetophenone in ethyl acrylate after 3 days at 65 °C. In contrast, tungsten hexacarbonyl is not an effective catalyst for cyclopropanation; 1,3-dipolar addition that results in the formation of stable 2-pyrazolines is dominant. The facility with which molybdenum hexacarbonyl promotes cyclopropanation is consistent with the relative ease for displacement of a carbonyl ligand from carbonyl complexes of elements in the chromium triad.[16]

The preliminary results that we report demonstrate the catalytic effectiveness of molybdenum hexacarbonyl for cyclopropanations of conjugated esters and nitriles. However, cyclopropane compounds are not formed from diazocarbonyl reactants in styrene or cyclohexene at 65 °C or in ethyl vinyl ether at its reflux temperature, even after 3 days in the presence of molybdenum hexacarbonyl. This substrate reactivity suggests that the reactive intermediate in these reactions possesses appreciable nucleophilic character.

Recently, Gassman has proposed consideration of a spectrum of reactive metal–carbene complexes ranging from those having electrophilic character to complexes with significant nucleophilic character.[17] The nucleophilic character of tantalum- and niobium-alkylidene complexes has been demonstrated,[18] and selective trapping of metal–carbene intermediates in metathesis reactions of phenyltungsten trichloride–aluminum chloride by the Michael acceptor ethyl acrylate has been observed.[17a] However, pentacarbonylmolybdenum–carbene complexes react with a wide variety of olefins by electrophilic attack of the carbene complex.[19] In contrast, the results that we have obtained suggest a molybdenum–carbene intermediate possessing definite catalytic activity for nucleophilic reactions. Further definitions of these reactions are under investigation.

**Acknowledgment.** We are grateful to the National Science Foundation for their support of this research. We thank Dr. Steven Bertz for helpful discussions.

**Registry No.** (E)-1 (R = $C_6H_5$, R′ = CN, Z = H), 64390-09-6; (Z)-1 (R = $C_6H_5$, R′ = CN, Z = H), 64390-08-5; (E)-1 (R = OEt, R′ = CN, Z = H), 3999-56-2; (Z)-1 (R = OEt, R′ = CN, Z = H), 699-23-0; (E)-1 (R = $C_6H_5$, R′ = CN, Z = $CH_3$), 73178-39-9; (Z)-1 (R = $C_6H_5$, R′ = CN, Z = $CH_3$), 73178-40-2; (E)-1 (R = OEt, R′ = CN, Z = $CH_3$), 73178-41-3; (Z)-1 (R = OEt, R′ = CN, Z = $CH_3$), 73178-42-4; (E)-1 (R = $C_6H_5$, R′ = COOEt, Z = H), 1518-20-3; (Z)-1 (R = $C_6H_5$, R′ = COOEt, Z = H), 15982-18-0; (E)-1 (R = OEt, R′ = COOEt, Z = H), 3999-55-1; (Z)-1 (R = OEt, R′ = COOEt, Z = H), 710-43-0; acrylonitrile, 107-13-1; methacrylonitrile, 126-98-7; ethyl acrylate, 140-88-5; α-diazoacetophenone, 3282-32-4; ethyl diazoacetate, 623-73-4; molybdenum hexacarbonyl, 13939-06-5; diethyl (E)-glutaconate, 73178-43-5; diethyl (Z)-glutaconate, 73192-75-3; 4-benzoyl-2-methyl-2-butenenitrile, 58422-86-9; diethyl fumarate, 623-91-6; diethyl maleate, 141-05-9; dibenzoylethylene, 4070-75-1.

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(12) Since significant amounts of $Mo(CO)_6$ are recovered during product isolation and the metal hexacarbonyl is reported to be produced from carbene ligand transfer to unsaturated esters,[9] we are not yet able to report the catalytic efficiency of molybdenum hexacarbonyl for these reactions. However, for reactions performed at 65 °C, cyclopropanation of acrylonitrile occurs effectively even when $Mo(CO)_6$ is employed in less than 1.0 mol %.

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