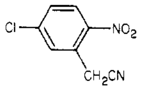
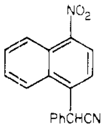
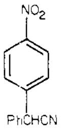
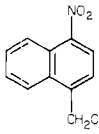
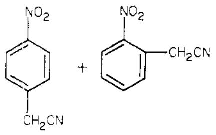
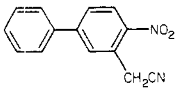
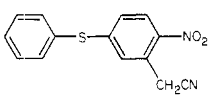
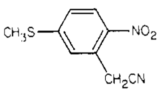
Table I

$$\mathrm{RCHXCN} + \mathrm{O_2NArH} \xrightarrow[\text{(2) HCl, }H_2O]{\text{(1) NaOH/Me}_2\text{SO}} \mathrm{O_2NArCHRCN} + \mathrm{XH}$$

R	X	$O_2N{-}Ar{-}\underset{R}{\underset{\vert}{C}}H{-}CN$	yield,[a] %	mp, °C
H	Cl		40	94-95.5
Ph	PhO		77	117-121
Ph	2,4-$Cl_2C_6H_3O$		57	69-71[b]
H	Cl		75	118-121
H	CH_3S		75	
H	PhS		80	
H	PhS		50[c] p 18 o	114-116[d] 82-83[d]
H	PhS		74	123-124
H	PhS		74	104-105
H	$(CH_3)_2NCS_2$		40	90-93

[a] All new compounds gave satisfactory microanalyses. These structures were established by IR and NMR spectra. Yields are given for isolated compounds. [b] Lit. mp 70-72 °C (R. B. Davis, L. C. Pizzini, *J. Org. Chem.*, 25, 1884 (1960). [c] Determined by GLC. [d] Lit. mp p 116 °C, o 81.5-82.5 °C (J. R. Knowles, R. Norman, *J. Chem. Soc.*, 2938 (1961).

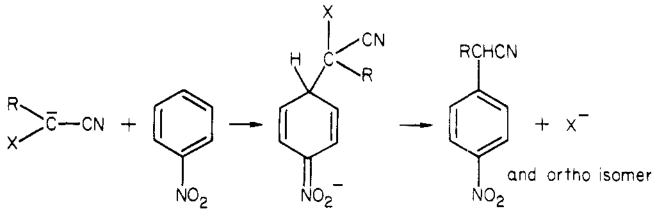
stituents; hence, they are much stronger C–H acids than the starting nitriles. In the reaction mixture they exist as corresponding carbanions; hence, the process should be carried out in the presence of at least 2 equiv of base (Scheme II).

Thus, when *S*-phenylthioglycolonitrile and nitrobenzene in Me_2SO solution were treated with an excess of powdered NaOH, an exothermic reaction accompanied by strong coloration of the mixture occurred. The reaction was carried out at 30 °C for 1.5 h; then dilution with water and acidification yielded a mixture of ortho and para isomers of nitrophenylacetonitrile, total yield 68%. Similarly from α-(2,4-dichlorophenoxy)phenylacetonitrile, phenyl(*p*-nitrophenyl)acetonitrile was obtained in 57% yield. No ortho isomer was observed in this case.

The examples of vicarious substitution of hydrogen by various α-substituted acetonitrile derivatives are given in Table I.

Vicarious substitution of hydrogen in aromatic nitro compounds with acetonitrile derivatives, besides being of mechanistic interest, offers a very practical synthetic approach of considerable utility. Although some of these products are easily prepared by other routes (e.g., nitration or nitroarylation of phenylacetonitrile), there are many compounds, particularly those containing a cyanomethyl group ortho to the nitro group, which cannot be easily prepared in other ways. The utility of these compounds as versatile starting materials in the synthesis of heterocycles is well established.[3]

Scheme II



R = H; X = PhS, MeS, $(CH_3)_2NCS_2$
R = Ph; X = PhO

Finally, we wish to comment on the probable mechanism of this reaction. Since we investigated these reactions with a preconception of the probable reaction pathway, we suppose that the transformation of the intermediate σ complex into the product proceeds via migration of the hydride anion to the carbon atom from which the "vicarious" leaving group departs (as shown in Scheme II). This general scheme illustrates our preconceivable mechanism; clearly, this is a tentative but consistent explanation of the reaction course. There are of course alternative mechanisms of worthy consideration; particularly, E2 type elimination from the intermediate would also be reasonable. A detailed mechanistic study is presently under way in our laboratory and will be reported in the future.

Acknowledgment. We express our thanks to the National Science Foundation for support of this research (Grant INT-14966).

Registry No. Chloroacetonitrile, 107-14-2; phenoxyphenylacetonitrile, 32121-27-0; α-(2,4-dichlorophenoxy)phenylacetonitrile, 72301-64-5; *S*-methylthioglycolonitrile, 35120-10-6; *S*-phenylthioglycolonitrile, 5219-61-4; *S*-(dimethylthiocarbamoyl)thioglycolonitrile, 61540-35-0; α-(5-chloro-2-nitrophenyl)acetonitrile, 72301-65-6; α-(4-nitro-1-naphthalenyl)phenylacetonitrile, 72301-66-7; phenyl(*p*-nitrophenyl)acetonitrile, 7599-05-5; 4-nitro-1-naphthaleneacetonitrile, 72301-67-8; *p*-nitrophenylacetonitrile, 555-21-5; *o*-nitrophenylacetonitrile, 610-66-2; 4-nitro-3-biphenylacetonitrile, 72301-68-9; α-[2-nitro-5-(phenylthio)phenyl]acetonitrile, 72301-69-0; α-[2-nitro-5-(methylthio)phenyl]acetonitrile, 72301-70-3; 1-nitronaphthalene, 86-57-7; 4-chloronitrobenzene, 100-00-5; nitrobenzene, 98-95-3; 4-nitrobiphenyl, 92-93-3.

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(3) I. D. London and G. Tennant, *Q. Rev., Chem. Soc.*, 18, 389 (1964). P. N. Preston and G. Tennant, *Chem. Rev.*, 72, 627 (1972).

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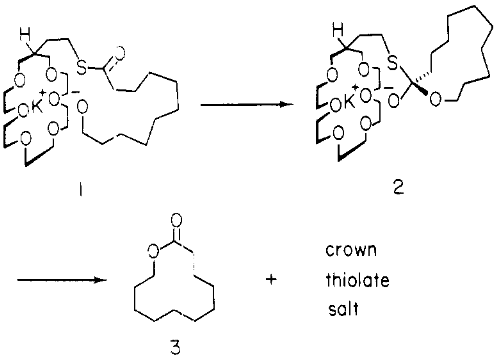
Transition-State-Stabilized Macrolide Closures

Summary: Thiol-functionalized crown ethers serve as reagents for macrolide closures. The thioesters derived from these crown ethers and ω-hydroxy carboxylic acids yield macrolides when treated with potassium *tert*-butoxide. The reaction proceeds via a templated conformation in which the ω-alkoxide is held proximate to the thioester

0022-3263/80/1945-1535$01.00/0

Scheme I



through ionic bonding to the crown-bound potassium cation. Variations in crown ether structure show that the criterion of proximate binding is necessary but not sufficient to ensure efficient macrolide closure. The optimal crown ether reagent provides transition-state stabilization for the attack of the alkoxide on the thioester carbonyl by situating the carbonyl oxygen immediately adjacent to the crown-bound potassium cation.

Sir: The closure of macrolides, particularly by ester bond formation, has received intense attention.[1] Recently we reported[2] the generation of templated alkoxide **1** which readily undergoes intramolecular cyclization (**1** → **2**) and subsequent collapse to undecanolide **3** and crown ether–potassium thiolate salt (Scheme I). We attributed the successful cyclization of **1** to the proximate binding of the alkoxide and thioester functionalities. Thus, we had reasoned that the *entropic* disadvantage of macrolide closure would not be manifested in **1** where appreciable *enthalpic* advantage would be associated with preclosure conformations (e.g., **1**) having small separations of the potassium cation and alkoxide anion.

Herein we report our continued study of crown ether, template-driven, macrolide closures and suggest that the criterion of proximate binding is necessary but not sufficient to ensure efficient macrolide closure. Evidence presented below points to intramolecular catalysis in **1** which stabilizes the transition state for ring closure (**1** → **2**).

In our previously communicated study,[2] crown thioester **4a** when treated under medium-dilution conditions with potassium *tert*-butoxide (Table I, entry 1) produced undecanolide **3** in 44% yield. Control cyclizations with ethyl thioester **6a** gave **3** in 5% yield in the presence of 19-crown-6 (Table I, entry 3) and in approximately 1% yield in the absence of added 19-crown-6.[2] The advantage of the crown ether reagent (**4a**) over the ethyl thioester (**6a**) is diminished but still significant at high dilution where higher yields are obtained from both thioesters (see Table I).

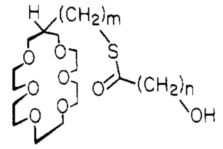
In the present work an assessment of the advantage gained by the crown ether templating effect for various macrolide ring sizes and for two crown ether series (**4a–f**[2] and **5a–f**[3]) has been made at medium dilution where any advantage of crown-mediated closure will be manifested.[4]

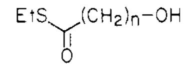
Table I

entry no.	thio- ester[a]	macro- lide ring size	macrolide[b] yield[c-e] medium dilution[g]	macrolide[b] yield[c-e] high dilution[h]	diolide[f] yield[c-e] at high dilution[h]
1	**4a**	12	44	72 (68)	(14)
2	**5a**	12	9–10		
3	**6a**[i]	12	5	57	
4	**4b**	13	37–47	64–77 (71–74)	(6)
5	**5b**	13	4–6		
6	**6b**[i]	13	9		
7	**4c**	16	57–58	73–76 (73–74)	(6)
8	**5c**	16	38–45		
9	**6c**[i]	16	40–43		
10	**4d**	7	25	19–23	19 (14)
11	**5d**	7	23–24		
12	**6d**[i]	7	27		
13	**4e**	8	0–1	0–1	37–41 (23)
14	**5e**	8	<1		
15	**6e**[i]	8	0		
16	**4f**	9	4	35	(27)
17	**5f**	9	0		

[a] Thioesters synthesized as described in ref 2 displayed satisfactory spectral data. [b] Macrolides were identified by their TLC and GLC behavior vs. that of authentic samples and displayed satisfactory spectral data. [c] Yield determined by GLC vs. internal standard. [d] Range represents yields from multiple reactions. [e] Yields in parentheses are isolated yields. [f] Diolides were identified by their TLC behavior vs. that of authentic samples and displayed satisfactory spectral data. [g] Thioester (~0.5 mmol) in benzene (~16 mL) and *t*-BuOK (1.05 equiv) in tetrahydrofuran (~16 mL) were simultaneously injected into ambient-temperature tetrahydrofuran (20 mL) over 10 h.[2] [h] Thioester (~0.5 mmol) in benzene (~16 mL) and *t*-BuOK (1.05 equiv) in tetrahydrofuran (~16 mL) were simultaneously injected into ambient-temperature tetrahydrofuran (~30 mL) contained in a high-dilution head over 3 h.[2] [i] The control ethyl thioester was injected along with 19-crown-6.[2]

As controls, thioesters **6a–e** have been cyclized at medium dilution in the presence of 19-crown-6[2] which will template the derived potassium alkoxides without organizing the ω-alkoxy methylene chains as in **1**.





4a, m = 2, n = 10	5a, m = 1, n = 10	6a, n = 10
4b, m = 2, n = 11	5b, m = 1, n = 11	6b, n = 11
4c, m = 2, n = 14	5c, m = 1, n = 14	6c, n = 14
4d, m = 2, n = 5	5d, m = 1, n = 5	6d, n = 5
4e, m = 2, n = 6	5e, m = 1, n = 6	6e, n = 6
4f, m = 2, n = 7	5f, m = 1, n = 7	

The crown thioester derived potassium alkoxides from **4** and **5** prior to cyclization are expected to adopt monomeric templated conformations (e.g., **1**) or form oligomeric ionic clusters. The equilibrium between monomeric and oligomeric alkoxide complexes will depend on the strain manifested in each type of complex upon close approach of alkoxide and potassium counterions and on the extent of derived ionic stabilization (enthalpic factors). The degrees of freedom lost in solution upon ionic oligomerization of alkoxide monomers will also play an im-

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(1) Reviews: (a) Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. (b) Back, T. G. *Ibid.* **1977**, *33*, 3041. (c) Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585.

(2) Rastetter, W. H.; Phillion, D. P. *Tetrahedron Lett.* **1979**, 1469.

(3) Hydroxy thioesters **5a–f** were produced from the corresponding mercapto crown ether by the procedure described in ref 2. The mercapto crown ether was made by $LiAlH_4$ reduction of the thioacetate produced by photochemical addition of CH_3COSH to the crown ether: Tomoi, M.; Abe, O.; Ikeda, M.; Kihara, K.; Kakiuchi, H. *Tetrahedron Lett.* **1978**, 3031.

(4) In principle, at the limit of *infinite dilution* **4a**, **5a**, and **6a** will close to equal yields of macrolide **3**.

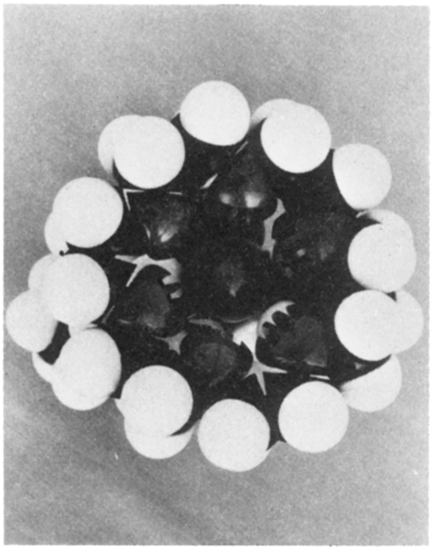

Figure 2. CPK model of tetrahedral intermediate **2**, viewed from below the plane of the crown ether. The potassium cation has been removed to show the alkoxide oxygen, previously the carbonyl oxygen of **1**, held directly over the potassium binding site. The ring of methylenes, now formed in **2**, is partially seen to the left and behind the crown ether.

portant role in this equilibrium (concentration-dependent entropic factors). The ratio of macrolide to diolide and other polyesters formed from the crown alkoxide salts will depend on the extent of ionic oligomerization and on the rate of attack on thioesters in the monomeric and oligomeric complexes.

Our results from the thioester series **4**–**6** are presented in Table I. Crown ether thioesters **4a**–**c** close to 12-, 13-, and 16-membered macrolides, respectively. Some degree of alkoxide oligomerization at medium dilution is likely responsible for the increased yield of macrolides with increased dilution. At medium dilution the yields from **4a**–**c** show facile ring closures as compared to the shorter crown homologues **5a**–**c** or the ethyl thioesters **6a**–**c**. The advantage seen in **4a**–**c** cannot be due entirely to the proximate binding of the thioesters and derived alkoxides as no advantage of crown series **5** over ethyl thioester series **6** can be discerned. An inspection of Corey–Pauling–Koltun (CPK) models reveals a mechanism for catalysis of ring closure (**1** → **2**) which is thought to operate in **4a**–**c** but not in the series **5a**–**c** or **6a**–**c**. As the alkoxide of **1** approaches the thioester carbonyl, negative charge density will begin to appear on the carbonyl oxygen. In tetrahedral intermediate **2** the negative charge is fully developed on the oxygen which occupied the carbonyl position in **1**. The rate of ring closure **1** → **2** will depend directly on the amount of ionic stabilization in the transition state for the process. Specifically, the transition state is characterized by negative charge density on *both* the alkoxide and carbonyl oxygens—both oxygens must be capable of close approach to the potassium cation to optimize transition-state stabilization.

The geometries of **4a**–**c** allow close approach of both oxygens to the counterion during each closure process. This is appreciated by inspection of Figure 1[5] which shows preclosure intermediate **1** and Figure 2 which shows tetrahedral intermediate **2**. The model of **2** shows clearly the templated alkoxide oxygen of the tetrahedral intermediate. The alkoxide of **2** provides a cap for the potassium binding site and is seen in the photograph (Figure 2) centered over the vacant site (K^+ removed from model). The chain of two methylenes which connects the sulfur atom in **2** to the crown is the correct length to allow the alkoxide and potassium counterions to touch *without disrupting* the inward-pointing orientation of the crown ether oxygens. The ionic stabilization seen in **2** will also be manifested in the transition state leading from **1** to **2**.

The ionic stabilization described for the closure **1** → **2** (for **4a**–**c**) will not be achieved easily for **5a**–**c**. A CPK model clearly shows that the methylene chain connecting the sulfur atom in **5a**–**c** to the crown ether is too short to allow placement of the alkoxide of the tetrahedral intermediate over the potassium binding site without pushing the collar of crown ether oxygens away from the bound cation (compare Figure 2). Thus, the closures in the series **5a**–**c** will proceed disrupting the geometry of the crown ether–potassium complex, or, alternatively, with increased charge separation between the developing alkoxide and the counterion.

The closure of ethyl thioesters **6a**–**c** in the presence of unfunctionalized crown ether (Table I) will occur only at the expense of the degrees of freedom associated with the floppy methylene chains. By contrast, the closure **1** → **2** does not require the random collision of alkoxide and thioester.

Successful macrolide production in the series **4a**–**f** is limited to large ring sizes. No advantage is seen for the use of **4d** or **4e** for closure of 7- or 8-membered macrolides, respectively, and only a slight advantage may exist for the 9-membered ring closure from **4f**. The failure of the template approach for these rings sizes, in part, may be due to product instability to closure conditions. In control experiments the 7-, 8-, 9-, and 12-membered macrolides were stirred with potassium ethyl thiolate and unfunctionalized 19-crown-6[2] under conditions of medium dilution macrolide closures (see Table I). Only 11-undecanolide was entirely stable to these conditions. Strained 7-heptanolide was completely destroyed by crown-bound ethyl thiolate overnight at ambient temperature; 6-hexanolide and 8-octanolide were 29%[6] and 83% recovered (GLC vs. internal standard), respectively, under these conditions. Thus, the failure of the template approach to medium ring sizes, in part, may be attributed to crown-catalyzed oligomerization of *formed* macrolides. However, it is also possible that the closures of monomeric templated alkoxides leading to medium-sized lactones are slow and the polyesters produced (e.g., the diolides) are largely kinetic products.

The current results with crown ethers **4** and **5** provide further examples of the predictive power[7] of CPK models in determining crown–substrate properties. We will further test our crown catalytic hypothesis (vide supra) by the design and building of a second crown ether which is also expected to provide transition-state stabilization during macrolide closure.

Acknowledgment is made to the National Institutes of Health for support of this work (Grant No. RO1 CA

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(5) Supplementary material.

(6) 6-Hexanolide was completely destroyed by further stirring (1 additional day) with the crown–potassium thiolate complex; the corresponding diolide was stable to these conditions. The yields for 6-hexanolide in Table I (entries 10–12) presumably reflect partial destruction of the product by the product thiolate salts (yields not optimized).

(7) Some success has been achieved with CPK models in predicting crown–substrate properties. See, e.g.: (a) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6754. (b) Stoddart, J. F. *Chem. Soc. Rev.* **1979**, *8*, 85. (c) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8. (d) Cram, D. J. *Techn. Chem. (N.Y.)* **1976**, *10*, Chapter, 5. (e) Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803.

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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Received January 3, 1980

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.

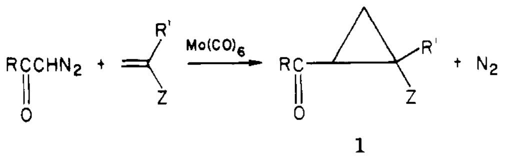
Sir: The cyclopropanation of unsaturated compounds by methylene and methine synthons has been a subject of intense interest, and numerous methodologies have been developed for this addition transformation.[1] Metal-catalyzed addition processes between diazo compounds and unsaturated substrates that occur 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 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



(1)

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