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Catalytic Role of Copper Triflate in Lewis Acid Promoted Reactions of Diazo Compounds

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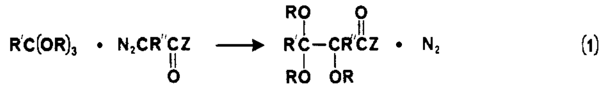
Copper(II) trifluoromethanesulfonate is often a superior catalyst for transformations of diazo compounds that are normally promoted by boron trifluoride etherate. Formal carbon–oxygen insertion occurs when ortho esters are reacted with diazocarbonyl compounds in the presence of $Cu(OTf)_2$, although the use of $BF_3{\cdot}Et_2O$ provides higher yields of the insertion products. In contrast, the β,γ-unsaturated diazo ketone **6** undergoes intramolecular cyclization to produce the corresponding cyclopentenone in higher yield with $Cu(OTf)_2$ catalysis than with the use of $BF_3{\cdot}Et_2O$. Intramolecular cyclopropanation of the γ,δ-unsaturated diazo ketone **8** occurs in exceptionally high yield in the presence of $Cu(OTf)_2$, whereas with $BF_3{\cdot}Et_2O$ intramolecular cyclization occurs with extensive rearrangement and fluoride transfer. Copper(II) triflate is unique among transition-metal catalysts that are normally employed for reactions with diazo compounds in its effectiveness for these transformations.

Copper(II) trifluoromethanesulfonate, $Cu(OTf)_2$, is widely recognized as an effective catalyst for reactions of diazo compounds with a variety of organic substrates.[1-3] Although its activity was originally demonstrated for cyclopropanation reactions,[1] $Cu(OTf)_2$ has also been employed for the selective formation of oxazoles from nitriles and diazo esters.[4] However, the production of oxazoles has been described as a Lewis acid promoted process,[5-7] whereas cyclopropane formation is associated with metal carbenoid intermediates.[3] Neither $Rh_2(OAc)_4$ nor $Rh_6(CO)_{16}$, both of which are exceptionally effective cyclopropanation catalysts,[8,9] offer comparable capabilities for oxazole formation.[10] The apparent dual role of $Cu(OTf)_2$ has prompted us to investigate the catalytic capability of copper(II) triflate in reactions of diazo compounds that are normally promoted by Lewis acids.

Results and Discussion

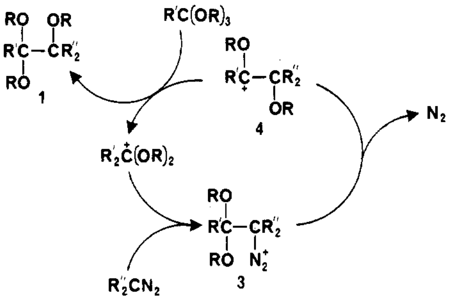
Ortho Ester Insertion. Schönberg and Praefcke have previously reported that diazo esters and diazo ketones undergo boron trifluoride etherate catalyzed carbenoid insertion with ortho esters (eq 1, R″ = H, Z = OEt, CH_3) and selected acetals.[11] These transformations are reported to be caused by addition of intermediate alkoxycarbenium ions to the diazo compound followed by dinitrogen extrusion and alkoxide transfer. We have found that the use of $Cu(OTf)_2$ in only 1.0 mol % based on diazo compound is effective for the production of insertion products with ortho esters (Table I). Byproducts of these reactions included the alcohol insertion product of the diazo compound (**2**, ROCHR″COZ), diethyl maleate and fumarate from reactions with ethyl diazoacetate, and, in the case of α-diazoacetophenone, α,α-dimethoxyacetophenone. The carbon–hydrogen insertion product from reactions with trimethyl orthoformate was not observed. By comparison with $Cu(OTf)_2$, $Rh_2(OAc)_4$ (Table I), $Rh_6(CO)_{16}$, $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, and $PdCl_2{\cdot}2PhCN$ were remarkably ineffective when employed under reaction conditions that caused dinitrogen extrusion from the diazo compound; yields of **1** from the use of these catalysts ranged from trace amounts to less than half those reported in Table I for $Rh_2(OAc)_4$. Neither trimethyl orthobenzoate nor 1,1,2,2-tetramethoxypropane underwent carbenoid insertion with either $Cu(OTf)_2$ or $BF_3{\cdot}Et_2O$; however, trimethyl orthobenzoate did undergo methoxide/methyl transfer to form methyl benzoate even in the absence of the diazo compound.



$$R'C(OR)_3 + N_2CR''\underset{\underset{O}{\|}}{C}Z \longrightarrow R'\underset{RO}{\overset{RO}{C}}-\underset{OR}{C}R''\overset{\overset{O}{\|}}{C}Z + N_2 \qquad (1)$$

1

Scheme I



Reaction conditions were optimized. However, increasing the time for addition of diazo compound to the reaction solution from 1 h to 8 h or increasing the amount of catalyst employed from 0.1 to 2.0 mol % had remarkably little effect on the yield of **1**. The use of ethyl ether as a solvent in reactions of trimethyl orthoformate with ethyl diazoacetate caused a substantial decrease in the yield of **1** without a significant increase in the yield of diethyl maleate and fumarate. The lack of sensitivity to changes in addition time and amount of catalyst is not character-

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Table I. Insertion Reactions of Diazo Compounds with Ortho Esters

ortho ester	diazo compd	catalyst	temp, °C	yield, % 1[a]	yield, % 2
$HC(OMe)_3$	$N_2CHCOOEt$	$Cu(OTf)_2$	25	45	6
		$Rh_2(OAc)_4$	25	20	27
		$BF_3 \cdot Et_2O$	25	83 (64)	5
	$N_2C(COOMe)_2$	$Cu(OTf)_2$	50	46	20
		$Rh_2(OAc)_4$	60	13	20
	$N_2CHCOPh$	$Cu(OTf)_2$	50	34	34[b]
		$BF_3 \cdot Et_2O$	25	58	4
$CH_3C(OEt)_3$	$N_2CHCOOEt$	$Cu(OTf)_2$	50	38[c]	15
		$Rh_2(OAc)_4$	50	3	11
		$BF_3 \cdot Et_2O$	40	(50)	
	$N_2C(COOMe)_2$	$Cu(OTf)_2$	50	<1	20
$CH_3CH_2C(OEt)_3$	$N_2CHCOOEt$	$Cu(OTf)_2$	60	<2	8
		$BF_3 \cdot Et_2O$	40	(46)	

[a] Yields in parentheses were taken from ref 11. [b] α,α-Dimethoxyacetophenone was produced in 15% yield. [c] Mixture of ethyl 2,3,3-triethoxybutanoate (20%) and ethyl 2-ethoxy-3-oxobutanoate (18%).

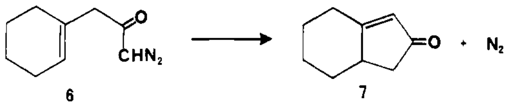
istic of either catalytic cyclopropanation reactions[9a] or of ylide generation and rearrangement with allyl substrates[12] and suggests that $Cu(OTf)_2$, in combination with diazo compounds,[13] produces dialkoxycarbenium ions which serve to propagate the formation of **1** (Scheme I). Alkoxy migration to the developing electrophilic center of **3** to produce **4** cannot be distinguished in the present study from direct displacement of dinitrogen by the ortho ester although, based on results from allyl acetal or aldehyde and ketone homologation reactions with diazo compounds,[14] the former pathway is more likely. Compounds **2**, which are produced in limited amounts in $BF_3 \cdot Et_2O$ promoted reactions but are generally major products in reactions catalyzed by transition metal compounds, suggest that initial formation of dialkoxycarbenium ions may be a consequence of alkoxide transfer to an electrophilic metal carbene (eq 2). Proton transfer to **5** or to the corresponding metal-dissociated enolate completes the formation of **2**. That $Rh_2(OAc)_4$ does not promote the decomposition of ortho esters and $Cu(OTf)_2$ is only moderately active towards ortho ester decomposition to carboxylate esters are consistent with this interpretation. However, the involvement of $Cu(OTf)_2$, either directly or through the production of protonic acid which subsequently adds to the diazo compound, in the generation of at least a portion of the propagating dialkoxycarbenium ions cannot be dismissed with available data for these ortho ester homologation reactions.

$$L_n\bar{M}-\overset{+}{C}R''_2 + R'C(OR)_3 \longrightarrow L_n\bar{M}-\underset{OR}{C}R''_2 + R'\overset{+}{C}(OR)_2 \quad (2)$$

5

Intramolecular Cyclization. Intramolecular cyclopropanation of γ,δ-unsaturated diazo ketones is well documented.[15] However, β,γ-unsaturated diazo ketones undergo skeletal rearrangement to γ,δ-unsaturated acid derivatives upon treatment with $CuSO_4$ or $Cu(acac)_2$,[16] whereas these same diazo ketones form cyclopentenones with the use of boron trifluoride etherate.[17] Rearrangement to γ,δ-unsaturated acid derivatives is believed to proceed through a carbenoid intermediate that undergoes intramolecular cyclization followed by structural rearrangement to a ketene intermediate,[16] whereas the acid-catalyzed transformation is reported to result from olefin addition by an intermediate vinyl cation.[17] Among the transition metal catalysts examined for ortho ester homologation and for oxazole formation,[4] $Cu(OTf)_2$ is superior to catalysts such as $Rh_2(OAc)_4$ or copper compounds traditionally employed for cyclopropane and ylide-forming reactions.[3,8-10] Consequently, $Cu(OTf)_2$ could be expected to facilitate intramolecular cyclization of β,γ-unsaturated diazo ketones in a manner like that of boron trifluoride etherate.

Treatment of diazo ketone **6** with $Cu(OTf)_2$ in nitromethane results in the formation of Δ^3-hydrinden-2-one (eq 3) in 59% yield, which should be compared to the 50% yield of this product obtained from **6** with the use of $BF_3 \cdot Et_2O$ under similar reaction conditions.[17b] In contrast, $Rh_2(OAc)_4$ is only moderately effective; the use of this catalyst results in a 26% yield of **7**. Solvent influences are pronounced; in ethyl ether compound **7** is formed in only 24% yield with the use of $Cu(OTf)_2$. Because of the nature of this transformation, the production of **7** could have been caused by the presence of a catalytic amount of protic acid. However, proton traps that could minimize the influence of protic acid also inhibit decomposition of the diazo compound by coordination with $Cu(OTf)_2$. Consequently, the divergence of the copper(II) triflate catalyzed conversion of **6** → **7** from the rearrangement pathway expected for copper-catalyzed reactions of **6** under entirely different conditions[16d] could not be explained for this system. Whatever the mechanism, however, $Cu(OTf)_2$ can be identified as particularly effective for the transformation of **6** → **7**.



6 7 (3)

To determine the limit of correspondence between $BF_3 \cdot Et_2O$ and $Cu(OTf)_2$, we examined the influence of catalysts for intramolecular cyclization of **8**. Copper catalysts have previously been reported to cause intramolecular cyclopropanation,[18] which would not be anticipated

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[13] The effective oxidation state of copper in these transformations is unknown but is inferred from prior investigations to be Cu(I).[1]

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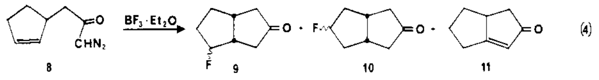
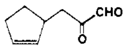
Table II. Catalyst/Solvent Influence on Product Compositions from Decompositions of Diazo Ketone 8

catalyst	solvent	temp, °C	yield, % 9	10	11	12	13	14
$BF_3 \cdot Et_2O$	CH_2Cl_2	0	29	24	12	<0.2		
	CH_3NO_2	0	2	1	1	19		
$Cu(OTf)_2$	CH_3NO_2	25					90	
	Et_2O	25					48	10
$Rh_2(OAc)_4$	CH_3NO_2	25					36	
	Et_2O	25					24	18

from $BF_3 \cdot Et_2O$ promoted reactions. With $BF_3 \cdot Et_2O$ in dichloromethane, 8 produced a surprisingly complex mixture of products (eq 4) that consisted mainly of the fluorobicyclooctanones **9** and **10**, as well as the bicyclooctenone **11**. In nitromethane the yields of **9** and **10** were insignificant, **11** was also a minor product, and **12** was the principal reaction product. In contrast, reactions performed with $Cu(OTf)_2$ in nitromethane produced the tricyclic ketone **13** in 90% yield. The yield of **13** was greatly reduced when these reactions were performed in ethyl ether due, in part, to competition by the solvent for capture of the electrophilic carbenoid intermediate that resulted in the formation of **14** (eq 5). In addition, catalysts that have been ordinarily more effective than $Cu(OTf)_2$ for cyclopropanation, particularly $Rh_2(OAc)_4$, produced **13** in significantly lower yields (Table II).



(4)



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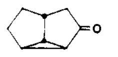

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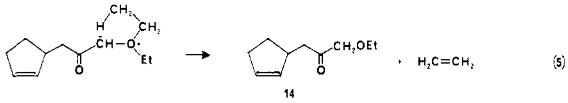
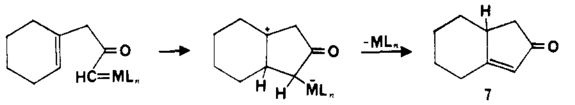


(5)

Successful Lewis acid promoted cyclization reactions of diazo ketones[17] have generally been characterized by generation of a tertiary carbenium ion. In these cases proton elimination completes product formation, although Wagner–Meerwein rearrangements are known to occur prior to elimination. In contrast, fluoride capture of intermediate carbocations is rare. Such transformations have not been previously observed in reactions of diazo ketones with $BF_3 \cdot Et_2O$, but they have been reported for a limited number of reactions in which fluoride is transferred from a complex fluoride anion to a relatively unstable carbocation.[19]

In the present case, **9** and **10** apparently arise by intermolecular fluoride transfer from a heteroatom associated fluoroborate, but the specific species involved in this transformation is undetermined. The conclusion that fluoride transfer is an intermolecular process is drawn from the low stereoselectivity for formation of **9** (isomer ratio = 1.8) and **10** (isomer ratio = 0.69). The tricyclic ketone **13** is stable toward $BF_3 \cdot Et_2O$ under the reaction conditions employed, but **13** undergoes slow structural rearrangement to **11** in low yield when heated with $BF_3 \cdot Et_2O$ in nitromethane at 80 °C.

Cyclopropanation is generally accepted as occurring through intermediate formation of a metal carbene species.[1a,3,8] Because of their structural similarity, both diazo compounds **6** and **8** should react with the catalytically active species to form intermediate electrophilic metal carbenes at similar rates. That $Cu(OTf)_2$ is effective for the conversion of **6** → **7** as well as of **8** → **13** clearly suggests that its activity is complex. The conversion of **6** → **7** may actually be a proton induced transformation, but this process can also be explained by intramolecular addition of an electrophilic metal carbene (eq 6).[20] That $Rh_2(OAc)_4$ is less effective than $Cu(OTf)_2$ for this transformation is consistent with the greater electrophilic character of the metal carbene derived from $Cu(OTf)_2$. This greater electrophilic character also explains the superior activity of $Cu(OTf)_2$ for oxazole formation[4] and for intramolecular cyclopropanation and suggests that $Cu(OTf)_2$ is the catalyst of choice for these transformations.



(6)

Experimental Section

Materials and Methods. Instrumentation has been previously described.[21] Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 2720 gas chromatograph with thermal conductivity detectors and on the Varian Vista 44 Gas Chromatography System with a flame ionization detector. Elemental analyses were performed by Galbraith Laboratories, Inc. Copper(II) triflate was prepared by the literature procedure.[22] Diazo ketones 6, 8, and α-diazoacetophenone were prepared from their corresponding acid chlorides and diazomethane.[23] Dimethyl diazomalonate was synthesized from dimethyl malonate and tosyl azide.[24] Solvents were rigorously dried according to standard procedures.

Reactions of Diazo Compounds with Ortho Esters. General Procedure. For reactions catalyzed by transition-metal compounds, the diazo compound (20.0 mmol) was added at a controlled rate over a 4-h period to a stirred mixture of the ortho ester (100 mmol) and transition metal catalyst (0.20 mmol) that was maintained under a nitrogen atmosphere. Reactions catalyzed by $BF_3 \cdot Et_2O$ were performed with 10.0 mmol of the diazo compound, 25.0 mmol of ortho ester, and 0.50 mmol of $BF_3 \cdot Et_2O$ according to the literature procedure.[11] α-Diazoacetophenone was dissolved in a portion of the ortho ester prior to its addition to the reaction mixture. After nitrogen evolution was complete, ether was added to the reaction solutions from $Cu(OTf)_2$ promoted reactions, and the ether solution was washed twice with a 25% aqueous solution of ethylenediamine. Reaction solutions from other transition metal promoted reactions were passed through a 3-cm column of neutral alumina with ether washings prior to extraction with aqueous sodium hydroxide. The resulting ether solution was dried over anhydrous magnesium sulfate, and the ether and excess ortho ester were distilled under reduced pressure. Yields were determined by GC analyses with the use of detector response values relative to the internal standard dibenzyl ether and were confirmed by ^1H NMR analyses. Physical properties of products derived from ethyl diazoacetate have been reported.[11b]

Ethyl 2,3,3-trimethoxypropanoate: ^1H NMR ($CDCl_3$) δ 4.54 (d, J = 5.8 Hz, $CH(OMe)_2$), 4.26 (q, J = 7.1 Hz, CH_2O), 3.84 (d, J = 5.8 Hz, $CHCOOEt$), 3.45 (s, OCH_3), 3.44 (s, OCH_3), 3.41 (s, OCH_3), 1.31 (t, J = 7.1 Hz, CH_3CH_2O); bp 140–142 °C (32 Torr) [lit.[11b] bp 100 °C (12 Torr)]. Anal. Calcd for $C_8H_{16}O_5$: C, 49.99; H, 8.39. Found: C, 50.23; H, 8.25.

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Methyl 2-carbomethoxy-2,3,3-trimethoxypropanoate: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.86 (s, $\mathrm{C}H(\mathrm{OMe})_2$), 3.83 (s, $\mathrm{COOCH_3}$, 6 H), 3.58 (s, $\mathrm{OCH_3}$), 3.55 (s, $\mathrm{OCH_3}$, 6 H); p 178–180 °C (32 Torr). Anal. Calcd for $\mathrm{C_9H_{16}O_7}$: C, 45.76; H, 6.83. Found: C, 45.54; H, 6.99.

1-Benzoyl-1,2,2-trimethoxyethane: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.20–8.00 (m, 2 H), 7.65–7.35 (m, 3 H), 4.67 (d, $J = 6.0$ Hz, 1 H), 4.53 (d, $J = 6.0$ Hz, 1 H), 3.50 (s, $\mathrm{OCH_3}$), 3.42 (s, $\mathrm{OCH_3}$), 3.30 (s, $\mathrm{OCH_3}$); mass spectrum, *m/e* (relative abundance) 193 (1.9, M – $\mathrm{CH_3O}$), 192 (11, M – $\mathrm{CH_3OH}$), 164 (3.2), 133 (3.1), 121 (4.5), 119 (2.9), 106 (4.7), 105 (52), 88 (13), 77 (47), 75 (100), 73 (14), 51 (18), 47 (14). Anal. Calcd for $\mathrm{C_{12}H_{16}O_4}$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.13.

Ethyl 2,3,3-triethoxybutanoate: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.24 (q, $J = 7.1$ Hz, $\mathrm{CH_3C}H_2\mathrm{OOC}$), 3.90–3.45 (m, 6 H), 3.79 (s, $\mathrm{C}H\mathrm{COOEt}$), 2.05 (s, $\mathrm{CH_3}$), 1.31 (t, $J = 7.1$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 1.29 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 1.27 (t, $J = 7.1$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 1.26 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$).

Acid catalysis transformed ethyl 2,3,3-triethoxybutanoate to ethyl 2-ethoxy-3-oxobutanoate: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.98 (s, $\mathrm{C}H\mathrm{COOEt}$), 4.12 (q, $J = 7.1$ Hz, $\mathrm{CH_3C}H_2\mathrm{OOC}$), 3.81 (q, $J = 7.0$ Hz, $\mathrm{CH_3C}H_2\mathrm{O}$), 2.28 (s, $\mathrm{CH_3}$), 1.33 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$), 1.26 (t, $J = 7.1$ Hz, $\mathrm{C}H_3\mathrm{CH_2OOC}$). Anal. Calcd for $\mathrm{C_8H_{14}O_4}$: C, 55.16; H, 8.10. Found: C, 55.03; H, 8.00.

Ethyl alkoxyacetates, methyl alkoxymalonates, α-methoxyacetophenone, and α,α-dimethoxyacetophenone were identified by ^{1}H NMR and mass spectral comparisons with authentic samples.

Copper(II) Triflate Catalyzed Decomposition of Diazo Ketone 6. Diazo ketone 6[25] (2.0 mmol) was added at a controlled rate over a 6-h period to a stirred pale blue solution of $\mathrm{Cu(OTf)_2}$ (0.040 mmol) in 5.0 mL of anhydrous nitromethane at 25 °C. After nitrogen evolution was complete, ether was added to the reaction solution, and the resulting solution was washed twice with a 25% aqueous solution of ethylenediamine. The resulting ether solution was dried over anhydrous magnesium sulfate, and the ether was distilled under reduced pressure to leave a residue containing a single volatile product identified as Δ^3-hydrindene-2-one by ^{1}H NMR[26] and mass spectral analyses. Reactions performed in ethyl ether yielded 1-cyclohexenyl-3-ethoxy-2-propanone (13%) in addition to 7.

Boron Trifluoride Etherate Catalyzed Decomposition of Diazo Ketone 8. Diazo ketone 8[18] (0.300 g, 2.0 mmol) in 100 mL of anhydrous dichloromethane was cooled to 0 °C and maintained under nitrogen. Boron trifluoride etherate (0.341 g, 2.4 mmol) was added, and the reaction solution was stirred at 0 °C for 2 h. The resultant gold-colored solution was washed with saturated aqueous sodium hydroxide and then dried over anhydrous magnesium sulfate. The solvent was distilled under reduced pressure. Reaction products were identified by ^{1}H NMR and mass spectral analyses of GC collected samples. Product yields were determined by capillary GC analyses on a 22-m Carbowax 20M column which provided baseline resolution of the isomeric fluorinated bicyclic ketones.

6-Fluorobicyclo[3.3.0]octan-3-one (9): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.21 (d of t, $J = 53.1$, 4.0 Hz, CHF of minor isomer), 4.91 (d of t, $J = 53.7$, 3.3 Hz, CHF of major isomer), 3.35–1.20 (m, 10 H); mass spectrum *m/e* (relative abundance) for major isomer, 144 (0.4, M + 2), 143 (4.1, M + 1), 142 (44, M), 127 (10), 122 (6), 113 (6), 99 (32), 95 (24), 94 (13), 86 (21), 85 (29), 81 (54), 80 (38), 79 (43), 77 (16), 73 (12), 72 (29), 68 (31), 67 (27), 66 (11), 65 (10), 59 (27), 57 (12), 56 (14), 55 (100), 54 (38), 53 (43), 51 (21); for minor isomer, 144 (0.9, M + 2), 143 (8.9, M + 1), 142 (100, M), 127 (23), 122 (15), 113 (15), 101 (11), 100 (22), 99 (84), 95 (31), 94 (27), 86 (21), 85 (32), 81 (34), 80 (41), 79 (74), 77 (20), 73 (30), 72 (62), 68 (30), 67 (28), 66 (11), 65 (11), 59 (12), 55 (22), 54 (21), 53 (50), 51 (19).

7-Fluorobicyclo[3.3.0]octan-3-one (10): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.22 (d of m, $J = 53.6$ Hz, CHF of major isomer), 5.08 (d of m, $J = 51.7$ Hz, CHF of minor isomer), 3.15–1.20 (m, 10 H); mass spectrum, *m/e* (relative abundance) for minor isomer, 144 (0.9, M + 2), 143 (9.4, M + 1), 142 (100, M), 127 (22), 122 (11), 113 (10), 99 (42), 95 (33), 94 (17), 86 (22), 85 (29), 81 (59), 80 (41), 79 (45), 77 (19), 73 (13), 72 (26), 68 (23), 67 (22), 65 (10), 59 (21), 55 (54), 54 (24), 53 (28), 51 (17); for major isomer, 144 (1.1, M + 2), 143 (8.9, M + 1), 142 (100, M), 127 (23), 122 (33), 113 (13), 100 (18), 99 (64), 95 (28), 94 (22), 91 (15), 86 (13), 85 (23), 81 (32), 80 (53), 79 (81), 77 (27), 73 (22), 72 (38), 68 (22), 67 (19), 66 (11), 65 (12), 55 (17), 54 (16), 53 (35), 51 (15).

Bicyclo[3.3.0]oct-1-en-3-one (11) was identified from its ^{1}H NMR spectrum[17b] and from its mass spectrum, *m/e* (relative abundance) 124 (0.3, M + 2), 123 (3.1, M + 1), 122 (32, M), 107 (6.5), 94 (5.1), 93 (7.4), 91 (7.4), 91 (8.3), 80 (63), (79 (100), 78 (13), 77 (37), 66 (14), 65 (12), 53 (14), 52 (11), 51 (18), 50 (12).

The α-dicarbonyl compound **12** was formed from reactions performed in nitromethane at 0 °C: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 10.2 (s, CHO), 5.90–5.55 (m, $\mathrm{CH{=}CH}$), 4.21 (d, $J = 4.6$ Hz, $\mathrm{CH_2CO}$), 3.09 (t, $J = 4.8$ Hz, $\mathrm{C}H\mathrm{CH_2CO}$), 2.52–2.00 (m, 3 H), 1.52–1.27 (m, 1 H); mass spectrum, *m/e* (relative abundance) 139 (0.4, M + 1), 138 (4.2, M), 109 (54, M – CHO), 81 (13), 79 (19), 77 (16), 67 (100), 66 (16), 65 (13), 53 (10), 51 (14).

Copper(II) Triflate Catalyzed Decomposition of Diazo Ketone 8. Diazo ketone 8 (0.30 g, 2.0 mmol) was added at a controlled rate over a 4-h period to a stirred pale blue solution of $\mathrm{Cu(OTf)_2}$ (0.014 g, 0.040 mmol) in 5.0 mL of anyhdrous nitromethane at 25 °C. After nitrogen evolution was complete, the reaction solution was worked up as previously described to produce tricyclo[3.3.0.0^{2,8}]octan-3-one (**13**) as the only volatile product (90% yield). When the same reaction was performed with 5.0 mmol of **6** in 10 mL of nitromethane, **13** was isolated by distillation in 81% yield: bp 40 °C (0.5 Torr) [lit.[18b] bp 76–77 °C (6.5 Torr)]. Reactions performed in ethyl ether yielded 1-cyclopentenyl-3-ethoxy-2-propanone (**14**) in addition to **13**: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.85–5.55 (m $\mathrm{CH{=}CH}$), 4.03 (s, $\mathrm{C}H_2\mathrm{OEt}$), 3.54 (q, $J = 7.0$ Hz, $\mathrm{CH_2O}$), 2.54–2.08 (m, 4 H), 1.54–1.32 (m, 1 H), 1.25 (t, $J = 7.0$ Hz, $\mathrm{C}H_3\mathrm{CH_2O}$); mass spectrum, *m/e* (relative abundance) 169 (0.2, M + 1), 168 (1.5, M), 122 (7.6), 109 (47), 80 (12), 79 (14), 67 (100), 66 (11), 59 (15).

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Registry No. **6**, 54495-73-7; **7**, 39163-29-6; **8**, 52898-44-9; **9**, 88969-19-1; **10**, 88969-20-4; **11**, 72200-41-0; **13**, 20826-85-1; **14**, 88969-21-5; $\mathrm{HC(OMe)_3}$, 149-73-5; $\mathrm{CH_3C(OEt)_3}$, 78-39-7; $\mathrm{CH_3CH_2C(OEt)_3}$, 115-80-0; $\mathrm{N_2CHCOOEt}$, 623-73-4; $\mathrm{N_2C(COOMe)_2}$, 6773-29-1; $\mathrm{N_2CHCOPh}$, 3282-32-4; $\mathrm{Rh_2(OAc)_4}$, 15956-28-2; $\mathrm{BF_3{\cdot}Et_2O}$, 109-63-7; ethyl 2,3,3-trimethoxypropanoate, 6085-14-9; methyl 2-carbomethoxy-2,3,3-trimethoxypropanoate, 88969-16-8; 1-benzoyl-1,2,2-trimethoxyethane, 88969-17-9; ethyl 2,3,3-triethoxybutanoate, 6085-15-0; ethyl 2-ethoxy-3-oxobutanoate, 88969-18-0; 1-cyclohexenyl-3-ethoxy-2-propane, 51149-72-5; α,α-dimethoxyacetophenone, 19159-39-8.

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