support given by the Department of Energy.

Registry No. **1**, 50-28-2; **1** 3-hypobromite derivative, 79769-51-0; **1** 3-phenoxy derivative, 79746-28-4; **2**, 15833-07-5; **3**, 1630-83-7; **4**, 19590-55-7; **5**, 57-63-6; **6**, 79746-29-5; **7**, 79746-30-8; **8**, 79769-52-1; NCS, 128-09-6; Br^-, 24959-67-9.

MIRC Reactions. 3. Use of Doubly Activated Substrates

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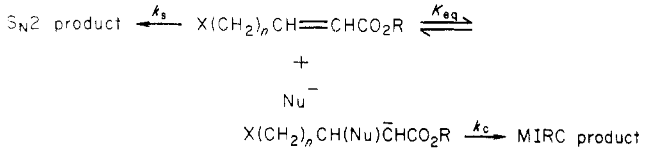
We recently reported the formation of three-, five-, six-, and seven-membered-ring esters bearing β-heteroatom substituents, through the utilization of what we have termed a MIRC (Michael Initiated Ring Closure) reaction.[1] Herein, we provide (1) a rationale for the use of geminate doubly activated ω-halo α,β-unsaturated esters rather than monoactivated systems as substrates for the MIRC reaction and (2) evidence which demonstrates that the doubly activated substrates constitute more desirable starting materials, in that both five- and six-membered-ring diesters can be prepared in fair to excellent yields by using a number of different nucleophiles, *including those which do not afford MIRC products when monoactivated systems are utilized.*

From our previous studies, we were aware that three-membered rings could be formed from the addition of lithium alkylthiolates to methyl 4-bromocrotonate in THF at 0 °C.[1] Five-, six-, and seven-membered rings were formed from the addition of lithium diisopropylamide (LDA) to the requisite ω-bromo α,β-unsaturated ester in THF at −78 °C (five- and six-membered ring) or at room temperature (seven-membered ring). However, attempts to close to five-, six-, and seven-membered rings by using alkylthiolates were thwarted by competitive S_N2 displacement reactions.[1b]

While this difference in behavior between nucleophiles was interesting to note, it was at the same time annoying, from the point of view that it appeared to point to a practical limitation upon the scope of the MIRC reaction. From the outset, we were particularly interested in being able to utilize a wide range of nucleophiles in order to take advantage of the chemistry associated with the carbon–nucleophile bond in the product and thereby modify it in a variety of potentially useful ways.[2] With this objective in mind, we initiated the study described below.

From an examination of Scheme I it is clear that the amount and the rate of formation of the MIRC product is dependent upon the enolate concentration and the rate constant for ring closure, k_c, while the amount and the rate of formation of the competing S_N2 product is dependent upon the concentration of the starting ester, the concentration of the nucleophile, and the rate constant for substitution, k_s. Obviously, the relative concentrations of the starting ester, the nucleophile, and the enolate are related to the equilibrium constant, K_{eq}.[3]

Scheme I



Scheme II. Thermodynamic Cycle to Estimate K_{eq}

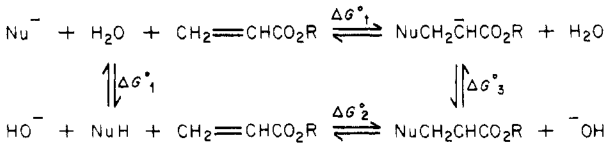
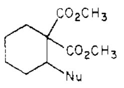
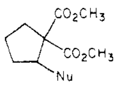


Table I[a]

% yield		nucleophile
		
46	65	L-Selectride
80	73	KCN
78	88	$NaCH(CO_2CH_3)_2$
94	82-94	*t*-BuSNa or Li

[a] See the Experimental Section for details. Yields refer to chromatographically pure compounds and are not optimized.

To gain an appreciation for the factors which influence the magnitude of K_{eq}, one can use the thermodynamic cycle which is illustrated in Scheme II. The individual steps associated with the cycle include two acid–base equilibria (steps one and three) for which, at 25 °C, $\Delta G°_1 = -1.37\Delta pK_a$ and $\Delta G°_3 = -1.37\Delta pK_a'$, where $\Delta pK_a = pK_a(NuH) - pK_a(H_2O)$ and $\Delta pK_a' = pK_a(H_2O) - pK_a(R'CH_2CO_2R)$, while for step two, $\Delta G°_2 = [\Delta H°(NuH) - \Delta H°(NuC)] + [\Delta H°(C{=}C) - \Delta H°(CH)] - T\Delta S°$. Thus, it follows that overall $\Delta G°_{total} = \Delta G°_t = \sum \Delta G°_i = [-1.37[pK_a(NuH) - pK_a(R'CH_2CO_2R)]] + [[\Delta H°(NuH) - \Delta H°(NuC)] + [\Delta H°(C{=}C) - \Delta H°(CH)] - T\Delta S°]$.

From these simple considerations, one can clearly see the role played by the pK_a difference between the conjugate acids of the nucleophile and the ester enolate upon the position of the overall equilibrium. Our objective was to make a reasonably minor perturbation to the original monoactivated substrate which would lead to a decrease in $\Delta G°_t$ relative to the monoactivated Michael acceptor system. To achieve this goal, we elected to utilize a doubly activated unsaturated ester (an alkylidene malonate) as the substrate since the pK_a of the conjugate acid of the enolate resulting after the conjugate addition is substancially lower than that of the monoactivated system and ought to thereby lead to a favorable shift in the equilibrium. Of course, simply shifting the equilibrium to the right does not guarantee the formation of a larger amount of the MIRC product, since changing from a less to a more highly stabilized enolate could lead to a reduction in the rate of ring closure, thereby still allowing the S_N2 process to compete favorably with the MIRC reaction.

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To test these ideas, we synthesized the five- and six-membered-ring precursors **1** and **2** according to the route illustrated below.[4]

$$XCH_2(CH_2)_nCHO \xrightarrow[\text{TiCl}_4\text{, pyr, } \text{CCl}_4/\text{THF}]{CH_2(CO_2CH_3)_2} XCH_2(CH_2)_nCH{=}C(CO_2CH_3)_2$$

1a, X = Cl; n = 2
b, X = Br; n = 2
c, X = Br; n = 3

As illustrated in Table I, good yields of both five- and six-membered-ring diesters were obtained by using a variety of different nucleophiles, some of which did not give rise to MIRC reaction products when the corresponding monoactivated ester was utilized.[1b] Of course, ring closure reactions involving ω-halomalonate anions have been known for many years and have been used on many occasions.[5] The significant feature of the present work has to do with the ability to couple a conjugate addition reaction, using a variety of different nucleophiles, to the ring closure reaction, a task which is not always so easy to accomplish.[6] It should also be noted that, in contrast with the results which we have previously observed in conjunction with the formation of cyclopropyl ring systems,[1a] there is no apparent counterion effect, viz., lithium, sodium, and potassium counterions can be utilized with equal effectiveness.

Additional studies, including an electrochemical variation of the MIRC reaction, are in progress.

Experimental Section[7]

Preparation of 4-Bromobutanal[8] and 5-Bromopentanal. To a three-necked, round-bottomed flask, cooled to 0 °C and equipped with an addition funnel and magnetic stirring bar, containing 1 equiv of either 4-bromobutyronitrile or 5-bromovaleronitrile (Aldrich) and enough ether to reach a concentration of ca. 1 M was added dropwise over 0.5 h 1.25 equiv of diisobutylaluminum hydride (20% solution in hexane). After the mixture was stirred at 0 °C for 2 h and at room temperature for 0.5 h, the reaction mixture was carefully added (foaming) to a precooled (0–5 °C) solution of 10% aqueous sulfuric acid. The resulting solution was stirred for 1 h, transferred to a separatory funnel, and extracted twice with ether. The combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to afford the crude aldehyde in yields ranging from 30% to 63%. The aldehydes could be distilled at reduced pressure; however, considerable decomposition occurs, and it is best to precede directly to the next step without purification. The spectral data for 5-bromopentanal were as follows: IR (neat) 2960, 2820, 2720, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.2 (t, 1 H, J = 2 Hz, CHO), 3.5 (t, 2 H, J = 4.5 Hz, CH_2Br), 2.6 (dt, 2 H, J = 6 and 2 Hz, CH_2CHO), m centered at 1.99 (4 H, CH_2). For 4-bromobutanal: IR (neat) 2955, 2825, 2725, 1725, 1432 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.8 (t, 1 H, J = 1 Hz, CHO), 3.45 (t, 2 H, J = 6 Hz, CH_2Br), 2.60 (dt, 2 H, J = 6 and 1 Hz, CH_2CHO), 2.2 (m, 2 H, CH_2).

Preparation of Alkylidenemalonates 1 and 2. To a three-necked round-bottomed flask equipped with an overhead stirrer and a nitrogen inlet tube and containing THF (enough so that after the addition of $TiCl_4/CCl_4$ the $TiCl_4$ concentration was 0.44 M) was cautiously added 2 equiv of a 4 M solution of titanium tetrachloride in carbon tetrachloride. The resulting cloudy yellow solution was stirred for 10 min after which 1 equiv each of the appropriate aldehyde and dimethyl malonate were added dropwise. This addition was immediately followed by the dropwise addition of 4 equiv of pyridine as a 5.76 M solution in THF. After the resulting brown solution was stirred for 60 h, the solution became beige (monitor by TLC). The reaction mixture was poured into an ice–water bath (bright yellow milky solution) and was then extracted with ether, washed with brine and saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated in vacuo to afford the crude product. The material was purified by using flash chromatography[9] (2/5 ether–pentane); yields of purified material ranged from 78% to 80%. Spectral data for **1b**: IR (neat) 3005, 2955, 1730, 1645, 1438 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.92 (t, 1 H, J = 8 Hz, vinyl), 3.83 (s, 3 H, CO_2CH_3), 3.77 (s, 3 H, CO_2CH_3), 3.37 (t, 2 H, J = 6 Hz, CH_2Br), 1.9–2.7 (m, 4 H, CH_2); exact mass calcd for $C_9H_{13}O_4{}^{79}Br$ 263.9996, found 263.9990; calcd for $C_9H_{13}O_4{}^{81}Br$ 265.9977, found 265.9976. For **2**: IR (neat) 1730, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0 (t, 1 H, J = 8 Hz, vinyl), 3.83 (s, 3 H, CO_2CH_3), 3.78 (s, 3 H, CO_2CH_3), 3.4 (t, 2 H, J = 4.5 Hz, CH_2Br), 1.6–2.6 (m, 6 H, CH_2). Anal. Calcd for $C_{10}H_{15}O_4Br$: C, 43.03; H, 5.41. Found: C, 42.80; H, 5.44.

MIRC Reactions with 2. To a dry 10-mL flask equipped with a magnetic stirring bar and a nitrogen inlet was added 200 mg (0.72 mmol) of **2** in 1.7 mL of anhydrous methyl alcohol. Except in the case of the potassium cyanide run where the substrate was added to a suspension of the KCN in methanol, 1.1 equiv of a 2 M solution of the desired nucleophile dissolved in anhydrous methyl alcohol was added dropwise via syringe.

For NaS-*t*-Bu. After 2 h at room temperature, the reaction mixture was washed with water, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Except for the reaction times which are specified for each case given below, the reaction workup proceeded along the same lines as that just given. For the thiolate run, the material was purified by using preparative TLC (E. Merck, silica gel 60 F_{254}, 2 mm; 2/5 ether–pentane). The spectral data were as follows: IR (neat) 2910, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.67 (s, 3 H, CO_2CH_3), 3.65 (s, 3 H, CO_2CH_3), 1.91 (m, 1 H, CH), 1.0–1.8 (m, 8 H, ring CH_2's), 1.26 (s, 9 H, *t*-Bu); exact mass calcd for $C_{14}H_{23}O_4S$ 288.1395, found 288.1395.

For KCN. After being stirred for 18 h at room temperature, the reaction mixture was worked up as described above. The material was purified by using preparative TLC with a mixture of 2/3 ether–pentane as the solvent. The spectral data were as follows: IR (neat) 2910, 2250, 1730, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, CO_2CH_3), 3.6 (m, 1 H, CH), 1.4–2.4 (m, 8 H, ring CH_2's); exact mass calcd for $C_{11}H_{15}O_4N$ 225.1013, found 225.1007.

For $NaCH(CO_2CH_3)_2$. After 3 h at room temperature, the reaction mixture was worked up as described above. Purification was accomplished by using preparative TLC with a mixture of 2/5 ether–pentane as the eluting solvent. The spectral data were as follows: IR (neat) 2910, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H, CO_2CH_3), 3.71 (s, 3 H, CO_2CH_3), 3.70 (s, 3 H, CO_2CH_3), 3.66 (s, 3 H, CO_2CH_3), 3.6 (m, 1 H, CH), 1.1–1.9 (m, 9 H, ring CH_2's). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.66; found: C, 54.25; H, 6.58.

MIRC Reactions with 1b. To a single-necked round-bottomed flask equipped with a nitrogen inlet and a magnetic stirrer was added a 0.5 M solution of **1b** (1 equiv) in dry THF. After the mixture was cooled in an ice bath, a 2 M solution of the nucleophile (1.05–1.1 equiv in THF) was added by using a syringe pump over a 30–45-min period; the ice bath was then removed.

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(7) Infrared, ^1H NMR, ^{13}C NMR, GLC, and GC/MS spectra were recorded with Perkin-Elmer 283, Varian T-60 or FT-80 (Me_4Si as an internal standard), Varian CFT-20 ($CDCl_3$ as an internal standard), Hewlett-Packard 5830A, and Hewlett-Packard 5992A instruments, respectively. Exact mass measurements were performed by using a ZAB 2-F spectrometer. Combustion analyses were carried out by the Marine Sciences Analytical Laboratories located at UCSB. THF was dried over calcium hydride and was freshly distilled from benzophenone ketyl prior to use.

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After the mixture was stirred at room temperature for 1-4 h (monitor via TLC), saturated aqueous ammonium chloride was added. The resulting solution was extracted twice with ether and once with pentane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated in vacuo.

For LiS-*t*-Bu. Purification via preparative TLC (same plates as described above) using 1/3 ether-pentane (three developments) was carried out. The spectral data were as follows: IR (neat) 2955, 2860, 1735, 1458, 1432, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, CO_2CH_3), 1.7-2.6 (m, 7 H, ring), 1.3 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 170.1, 168.9, 63.6, 53.9, 53.0, 35.8, 33.3, 30.7, 23.4; low-resolution mass spectrum, *m/e* 274, 217, 187, 158, 145, 126, 113, 95, 57; exact mass calcd for $C_{13}H_{22}SO_4$ 274.1239, found 274.1238.

For $NaCH(CO_2CH_3)_2$[10] the spectral data were as follows: IR (neat) 2955, 2850, 1735, 1438 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, CO_2CH_3), 3.38 (t, 1 H, J = 8 Hz, $CH(CO_2CH_3)_2$), 1.6-2.6 (m, 7 H, ring); ^{13}C NMR ($CDCl_3$) δ 168.9, 62.1, 54.1, 52.5, 52.2, 35.6, 22.2.

For KCN the spectral data were as follows: IR (neat) 2955, 2870, 2280, 1735, 1450, 1432 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H, CO_2CH_3), 3.78 (s, 3 H, CO_2CH_3), 1.7-2.8 (m, 7 H, ring); ^{13}C NMR ($CDCl_3$) δ 169.9 (CN), 53.2, 53.1, 35.8, 33.4, 30.8, 23.5; exact mass calcd for $C_{10}H_{14}NO_4$ [$(M + 1)^{+\cdot}$; as is sometimes the case for nitriles, the $M^{+\cdot}$ peak was not observed while the $(M + 1)^{+\cdot}$ was observed[11]) 212.0877, found 212.0914. High-resolution mass spectra on several key fragments include the following [*m/e* (relative intensity)]: calcd for $C_7H_8NO_4$ 170.0453 (100), found 170.0475; calcd for $C_2H_3O_2$ 59.0132 (95), found 59.0157; calcd for C_5H_7 67.0547 (79), found 67.0588; calcd for $C_9H_{10}NO_3$ 180.0661 (48), found 180.0695.

L-Selectride Reactions with 1b and 2.[14] To a two-necked round bottomed flask equipped with a nitrogen inlet and a magnetic stirring bar was added 1.1 equiv of L-Selectride (1 M solution in THF); the flask was then cooled to -78 °C. After 15 min, a 1 M solution of the substrate dissolved in THF was added by using a syringe pump over 30-45 min. The cooling bath was then removed and the solution was then raised to either 0 °C (for **1b**) or reflux (for **2**) for 1 h after which time the reaction was quenched by the addition of saturated aqueous ammonium chloride. After extraction of the aqueous layer with ether, the combined organic material was washed two times with brine, dried ($MgSO_4$), and concentrated in vacuo. The products were purified by using gravity-flow chromatography on silica gel (E. Merck, 70-230 mesh; 20% ether-pentane). For **2**:[12] IR (neat) 2955, 1720, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 6 H, CO_2CH_3), 1.8-2.2 (m, 4 H, $CH_2C(CO_2CH_3)_2CH_2$), 1.26-1.73 (m, 6 H, remaining ring H's); GC/MS *m/e* (relative intensity) 200, 169, 145, 132, 113, 108, 80 (100), 59. For **1b**:[13] IR (neat) 2955, 1730, 1435 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H, CO_2CH_3), 1.95-2.42 (m, 4 H, $CH_2C(CO_2CH_3)_2CH_2$), 1.46-1.93 (m, 4 H, remaining ring H's); ^{13}C NMR ($CDCl_3$) δ 172.3, 59.8, 51.7, 34.0, 24.8; GC/MS (parent not observed) *m/e* (relative intensity) 155, 145 (100), 126, 113, 95, 67, 59.

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Registry No. **1b**, 79917-27-4; **2**, 79917-28-5; 4-bromobutanal, 38694-47-2; 5-bromopentanal, 1191-30-6; 4-bromobutyronitrile, 5332-06-9; 5-bromovaleronitrile, 5414-21-1; dimethyl malonate, 108-59-8; 1,1-cyclohexane dicarboxylic acid dimethyl ester, 72963-31-6; 2-cyano-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-29-6; 2-[[bis(methoxycarbonyl)]methyl]-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-30-9; 2-(*tert*-butylthio)-1,1-cyclohexane dicarboxylic acid dimethyl ester, 79917-31-0; 1,1-cyclopentane dicarboxylic acid dimethyl ester, 74090-15-6; 2-cyano-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-32-1; 2-[[bis(methoxycarbonyl)]methyl]-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-33-2; 2-(*tert*-butylthio)-1,1-cyclopentane dicarboxylic acid dimethyl ester, 79917-34-3; L-Selectride, 38721-52-7; KCN, 151-50-8; $NaCH(CO_2CH_3)_2$, 18424-76-5; *t*-BuSNa, 29364-29-2; *t*-BuSLi, 16203-42-2.

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A New Triphasic Solid-Solid-Liquid Catalytic System for the Inexpensive and Selective Oxidation of Secondary Alcohols by Calcium Hypochlorite

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In the past decade, biphasic liquid-liquid and solid-liquid reactions have had a remarkable development, leading to the currently classical notion of "phase transfer catalyst" or "ionophore"; comprehensive theoretical interpretation has also been offered.[1] Among the four possible condensed triphasic systems, liquid-liquid-solid and liquid-solid-solid are of more recent and growing interest (see ref 2 and 3 and references mentioned herein), although they are not fully grasped yet. We report here an additional example of such a triphasic solid-solid-liquid catalysis, applied to the oxidation of alcohols by calcium hypochlorite in the presence of a solid polymer in a nonaqueous medium.

Sodium hypochlorite in acetic acid[4] or in a biphasic water-solvent system[5] has proven to be an efficient and economically interesting oxidation agent, although some difficulties may occur for the extraction of water-soluble ketones. The alternative proposed here, like previous research on the $KMnO_4$-$CuSO_4$ $(H_2O)_5$ pair,[3] makes it possible to work in an organic medium and to isolate the oxydation products through easy filtration and evaporation of the solvent. We used commercial calcium hypochlorite[6] in various solvents (CH_2Cl_2, CCl_4, Et_2O, CH_3CO_2Et) and catalytic amounts of a "hypochlorite" resin obtained from commercial IRA 900 (technical details are given in the Experimental Section).

Results are summarized in Table I. A separate run without a catalyst (entry 1) demonstrates a low activity of calcium hypochlorite alone, owing probably to the presence of traces of water.[3] Yields are not improved when working in the presence of the initial ammonium chloride

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