Ambident Reactivity of Medium-Ring Cycloalkane-1,3-dione Enolates[1]

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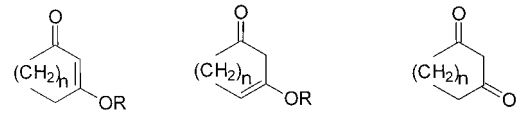
Cycloalkane-1,3-diones with ring sizes 7−10 have been converted to their enolates and subjected to a variety of ethylation and methylation reagent/solvent systems. The greatest amount of O-alkylation was encountered using ethyl tosylate in HMPA. The O/C alkylation ratios decreased with almost every reagent/solvent system as the ring size was increased. This trend is consistent with greater steric strain in the conjugated enolate resonance contributor, resulting in diminished O-attack as the ring size is increased.

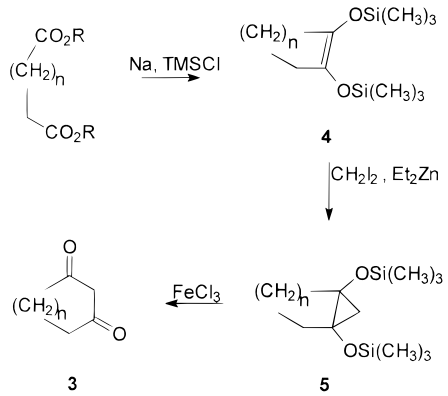
The ability of enols and enolate anions to function as ambident species is an important aspect in many synthetic applications.[2,3] For the enols and enolates derived from 1,3-diones, the understanding of ambident behavior is complicated by the various conformations of the enone segments and the contribution of chelated or intramolecularly hydrogen-bonded species.[2] As part of a study of enone equilibria in medium-ring cycloalkenones,[4] preparation of 7- to 10-membered 3-alkoxycycloalkenones (**1**, **2**) became essential in order to probe the effect of strongly electron-donating groups on these equilibria. If O-alkylation of cycloalkane-1,3-diones (**3**, $n = 3-6$) could be performed in high yield, the desired compounds could be prepared in a straightforward manner.



1 **2** **3**

The desired medium-ring cycloalkane-1,3-diones (**3**, $n = 3-6$) were prepared (Scheme 1) by the ring expansion method developed by Ito[5] for the 7- and 9-membered rings and modified by Pirrung[6] for the 8-membered ring.[7]

Scheme 1[5]



Since Pirrung[6] reported a 43% yield of 3-ethoxy-2-cyclooctenone (**1**, $n = 4$) using potassium *tert*-butoxide and triethyloxonium fluoroborate (TEO) in DME, initial attempts were addressed to using this system to O-alkylate the 10-membered dione (**3**, $n = 6$). The results were poor yields of a complex mixture of products. It was therefore decided to perform a more systematic investigation of the alkylation of these four 1,3-diones.

A starting point was the work of Sraga and Hrnciar,[8] who studied the methylation of the 5-, 6-, and 7-membered 1,3-diones. They reported that the ratio of O-methylated product to C-methylated product was much greater in the 5-membered ring than in the 6-membered ring and was greater in the 6-membered ring than in the 7-membered ring. They reported 57−65% total yields of 7-membered ring products, with 80% O-methylation from diazomethane in methanol and total O/C ratios[9] of 0.8, 0.2, 0.1, 0.2, and 0.9 using methyl iodide and anhydrous potassium carbonate in ether, THF, acetone, acetonitrile, and DMF, respectively. These results followed the expected trends.[2,3] Polar aprotic solvents increase O-alkylation, while nonpolar and hydrogen-bonding solvents decrease O-alkylation. The harder the electrophilic center in the alkylating agent, the greater the preference for O-alkylation.[10] Thus, leaving group effects for O-alkylation should be in the order iodide < bromide < chloride < tosylate < ether.[2]

(1) Taken from: Thompson, G. S. Ph.D. Dissertation, Seton Hall University, 1995.

(2) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin, Inc.: Menlo Park, CA, 1972; Chapter 9.

(3) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1983; Part B, Chapter 1.7.

(4) Eskola, P.; Hirsch, J. A. *J. Org. Chem.* **1997**, *62*, 5732 and previous papers in the series.

(5) Ito, Y.; Fujii, S.; Nakatsuka, M.; Kawamoto, F.; Saegusa, T. *Org. Synth.* **1979**, *59*, 113. Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073.

(6) Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3606.

(7) Other syntheses of **3**. $n = 3$: (a) Maclean, I.; Sneeden, R. P. A. *Tetrahedron* **1965**, *21*, 31. (b) Eistert, B.; Haupter, F.; Schank, K. *Justus Liebig Ann. Chem.* **1963**, *665*, 55. (c) Bhushan, V.; Chandrasekaran, S. *Synth. Commun.* **1984**, *14*, 339. $n = 3$, 4, and 8: (d) Suzuki, M.; Watanabe, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 2095. $n = 3-5$: (e) Nishiguchi, I.; Hirashima, T.; Shono, T.; Sasaki, M. *Chem. Lett.* **1981**, 551. $n = 4-8$: (f) Schank, K.; Eistert, B.; Felzmann, J. H. *Chem. Ber.* **1966**, *99*, 1414. Eistert, B.; Schank, K. *Tetrahedron Lett.* **1964**, *8*, 429. $n = 6$ and 7: (g) Beccalli, E. G.; Majori, L.; Marchesini, A. *J. Org. Chem.* **1981**, *46*, 222. $n = 7-11$ and 13: (h) Hunig, S.; Hoch, H. *Tetrahedron Lett.* **1966**, *42*, 5215; *Liebigs Ann. Chem.* **1968**, *716*, 68. (i) Kirrmann, A.; Wakselman, C. *Bull. Soc. Chim. Fr.* **1967**, *10*, 3772. $n = 11$: Reference 5. $n = 3-5$ with 2-methyl substituent: (j) Brooks, D. W.; Mazdiyasni, H.; Sallay, P. *J. Org. Chem.* **1985**, *50*, 3411.

(8) Sraga, J.; Hrnciar, P. *Chem. Zvesti* **1981**, *35*, 119.

(9) O/C ratios are the amount of 2-alkoxyenone (**1** + **2**) plus any 1,3-dialkoxydiene (**9**) relative to the total amount of 2-alkyl (**6**), 2,2-dialkyl (**7**), 2,2,4-trialkyl 1,3-dione (**10**), and 2-alkyl-3-alkoxy enone (**8**).

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Table 1. O/C Ratios for the Alkylation of Cyclodecane-1,3-dione (3, $n = 6$)

	O/C ratio[9] (% *O*-alkylated product[a])			
solvent	RI[b]	Me_2SO_4	Et tosylate	Et_3OBF_4
DME	<0.1 (4)	<0.1 (4)	0.1 (6)	1.6 (23)[c]
80%DME/20%HMPA	*d*	0.5 (27)	0.7 (38)	1.3 (35)
DMSO	<0.1 (1)	0.8 (38)	1.8 (61)	1.1 (33)
HMPA	0.1 (8)	1.9 (31)	3.1 (70)	0.9 (30)

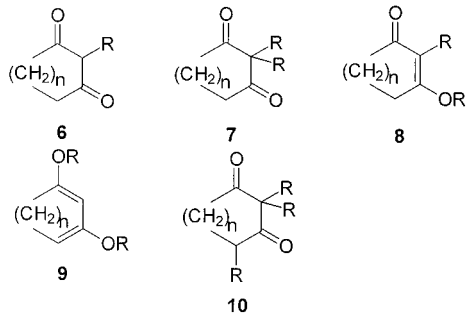
[a] *cis*-3-Ethoxy- or −3-methoxy-2-cyclodecenone (**1**, $n = 6$). [b] EtI or MeI. [c] Includes THF data. [d] Not determined.

Table 2. Alkylation of Cyclononane-1,3-dione (3, $n = 5$)

system (equiv)[a]	**3**[b]	**1**	**9**	**6**	**7**	O/C ratio[9]
DME/EtI (5X)	2	57	0.2	34	6	1.4
HMPA/EtI (10X)	3	38	0.1	44	15	0.6
HMPA/EtTos (2.5X)[c]	<1	88	0.7	4	2	15
HMPA/EtTos (2.3X)[d]	<1	89	4	3	3	16

[a] A solution of potassium *tert*-butoxide (1.1−1.2 equiv) was added to a stirred solution of cyclononane-1,3-dione (0.7 mmol) in 10 mL of solvent under N_2 at rt. The alkylating reagent was added after stirring for 15 min and the reaction monitored by GC. [b] Percent cyclononane-1,3-dione (**3**) remaining. [c] Reaction performed using 3.2 mmol dione. [d] Reaction performed using 6.3 mmol dione.

We chose to compare the reactions of ethyl iodide, methyl iodide, dimethyl sulfate, ethyl tosylate, and TEO in the presence of potassium *tert*-butoxide in DME, THF, DMSO, HMPA, and 80% DME/20% HMPA. The results for cyclodecane-1,3-dione (**3**, $n = 6$) are summarized in Table 1 (see the Supporting Information for details: Tables 5−8). Increasing solvent polarity (HMPA most polar)[11] produced significant increases in O-alkylation, especially with ethyl tosylate and dimethyl sulfate. The highest yield of the desired 3-alkoxycyclodecane-1,3-dione (**3**, $n = 6$) was obtained with ethyl tosylate in HMPA. Unexpectedly, TEO did not show this trend, nor were yields high. This was the result of the typical presence of about 40% of unreacted 1,3-dione starting material even when large amounts of TEO were utilized. On the other hand, the largest amount of 2-alkylated product (**6**, $n = 6$) was usually found with the alkyl iodide, and the largest amount of 2,2-dialkylated material (**7**, $n = 6$) was observed with either methyl iodide or dimethyl sulfate in DMSO, with the number of equivalents of base used being an additional variable in the formation of **7**.



Limited comparisons were performed in the 9-, 8-, and 7-membered rings (Tables 2−4, respectively), but the trends were similar. Ethyl tosylate in HMPA produced

Table 3. Alkylation of Cyclooctane-1,3-dione (3, $n = 4$)

system (equiv)[a]	**3**[b]	**1**	**6**	**7**	O/C ratio[9]
DME/EtI (5X)	6	54	21	17	1.4
DME/Et_3OBF_4 (1.2X)	11	77	4	0.1	19
THF/Et_3OBF_4 (1.2X)	1	80	5	0.2	15
HMPA/EtI (5X)		40	31	24	0.7
HMPA/EtTos (2.5X)[c]		90	2	0.5	36
HMPA/EtTos (2.5X)[c,d]		89	3	0.8	23

[a] A solution of potassium *tert*-butoxide (1.2 equiv) was added to a stirred solution of cyclooctane-1,3-dione (0.4−0.6 mmol) in 10 mL of solvent under N_2. The alkylating agent was added after 15 min of stirring and the reaction monitored by GC. All were at rt except Et_3OBF_4 were at 0°C. [b] Percent cyclooctane-1,3-dione remaining. [c] Product mixture contained 5% of an unknown component. [d] Reaction used 6.1 mmol of dione.

Table 4. Alkylation of Cycloheptane-1,3-dione (3, $n = 3$)

system (equiv)[a]	**3**[b]	**1**	**9**	**6**	**7**	**8**	O/C ratio[9]
DME/EtI (10X)[c]	45	43		12			3.6
DME/EtI (10X)[d]	3	67		4	16	5	2.4
HMPA/EtTos (2.5X)[d,e,f]	1	60	26	1		2	29
HMPA/EtTos (2.5X)[d,f]	2	50	29	1		5	13[f]
HMPA/EtTos (2.5X)[d,g,h]		1	70	1			*h*
THF/Et_3OBF_4 (3X)	49	36		2		0.5	18

[a] A solution of potassium *tert*-butoxide was added to a stirred solution of cycloheptane-1,3-dione (0.5 mmol) in 10 mL of solvent under N_2 at rt (at 0°C for Et_3OBF_4). Alkylating agent was added after 15 min stirring and the reaction monitored by GC. [b] Percent of cycloheptane-1,3-dione remaining. [c] 0.5 equiv of base. [d] 1.0 equiv of base. [e] Used 2.5 mmol of dione. [f] Contained two unidentified trialkylated products in 7.5% and 2% yield, which are ignored in calculating the O/C ratio. [g] Continuation of previous experiment with an additional 0.5 equiv of base added after 1.5 h. [h] Contained two unidentified trialkylated products corresponding to 19% and 4% yield.

approximately 90% of 3-ethoxy-2-cyclononenone (**1**, $n = 5$) and 3-ethoxy-2-cyclooctenone (**1**, $n = 4$) with O/C ratios[9] of 16 and 30, respectively. The results with ethyl tosylate/HMPA and cycloheptane-1,3-dione were complicated by the large amount of 1,3-diethoxy-1,3-cycloheptadiene (**9**, $n = 3$) formed. All of the reagent/solvent systems preferred O-alkylation in the 7-membered ring 1,3-dione.

One notable trend is the decrease in the O/C ratio with almost every reagent/solvent system as the ring size was increased. In the case of ethyl tosylate in HMPA, this ratio decreased from 30 in the 8-membered ring to 16 in the 9-membered ring to 3 in the 10-membered ring. As the ring size increases, the steric requirement to have a coplanar arrangement of a conjugated enone system becomes more severe. This results in an increasing preference for 3-cycloalkenones over 2-cycloalkenones[4,12] as ring size increases from 7 to 10. In the current work, the destabilization with increasing ring size of the conjugated enone resonance contributor **11** in the enolate anion from the 1,3-dione results in increasing importance of the carbon acid resonance contributor **12**. The result is greater C-alkylation with increasing ring size as long as the same reagent/solvent system is compared. These results also parallel the kinetic studies of Rhoads[11] on the isopropylation of 2-carbalkoxycycloalkanones with ring sizes 5−8 and 10, where the rates of attack on carbon relative to attack on oxygen in DMSO and in HMPA increased with increasing ring size. However, Rhoads' system involves different mixes of enolate conformations

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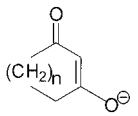
because one of their carbonyls is external to the ring. In addition, Rhoads pointed out the possibility of their working near the isokinetic temperature.



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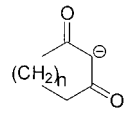

12

Experimental Section

The NMR spectra were obtained in solutions of deuteriochloroform ($CDCl_3$) with 0.03% tetramethylsilane (TMS) except for the trimethylsiloxy compounds, which were obtained in $CDCl_3$. Ultraviolet spectra were obtained in *n*-hexane (HPLC grade) unless otherwise noted. GC−MS data were obtained with a J&W DB-1 (30 m × 0.25 mm i.d., 0.25 μm film thickness) column or a Hewlett-Packard HP1 (12 m × 0.2 mm i.d., 0.33 μm film thickness) column. GC analyses were performed with a J&W DB-1 (30 m × 0.53 mm i.d., 5 μm film thickness) column, a J&W DB-1 (15 m × 0.555 mm i.d., 1.5 μm film thickness) column, or an XF1150 6 ft × 4 mm glass column. Elemental analysis was performed by Analytische Laboratorium, Elbach, Germany. Flash column chromatography was performed utilizing E. M. Sciences silica gel 60 (particle size 0.040−0.063 mm) with suitable solvents in glass columns with 1.5, 2, or 3 cm i.d. TLC analyses were performed on Merck silica gel 60 F254 precoated glass plates (layer thickness 0.25 mm) with detection by either shortwave UV, vanillin spray, or iodine chamber. All syntheses were performed using oven-dried glassware under a nitrogen atmosphere. Both DME and THF were distilled from Na/benzophenone prior to use, while DMF was stored over BaO and was distilled from either BaO or CaH_2 under reduced pressure (20 mmHg) prior to use. The DMSO was stored over BaO, distilled under reduced pressure, and further dried by refluxing over CaH_2 followed by distillation under reduced pressure. The HMPA was refluxed over BaO under reduced pressure with an N_2 atmosphere followed by distillation. The HMPA was then refluxed and distilled from Na under reduced pressure with an N_2 atmosphere. Toluene was refluxed and distilled from either Na or CaH_2 prior to use. Trimethylsilyl chloride (TMSCl) (Aldrich, 98%) was distilled from CaH_2 prior to use. Reagents were generally used as obtained from the supplier. Details on individual experiments are found in the Supporting Information.

General Procedure for the Synthesis of 1,2-Bis(trimethylsiloxy)cycloalkenes 4.[5,7j,13] A solution of the dimethylalkanediester in dried toluene was slowly added, dropwise, to a stirred solution of cleaned Na sand and TMSCl in dried toluene at the temperature specified in the individual procedure. The cleaned Na was prepared[14] by heating pieces of Na in toluene until melted and pouring the molten Na into dried toluene. The clean Na balls were easily separated from the oxidized Na residues. The Na sand[14] was prepared in the reaction flask by vigorously stirring (5−10 min) the weighed, clean Na balls in refluxing toluene until a fine suspension of Na was obtained. A Hershberg-type wire paddle was utilized to stir the Na. The heat was removed with continued stirring until the Na suspension solidified. After addition of the diester was complete, the stirred mixture was refluxed until the reaction was complete and then cooled to room temperature. Generally, the reaction turned deep purple upon addition of the diester. The mixture was vacuum-filtered using a sintered glass funnel, and the purple precipitate was rinsed with 100−200 mL of dried toluene. The precipitate, containing excess Na, was carefully treated with 2-propanol. The toluene was removed from the combined toluene filtrates at atmospheric or reduced pressure, and the residue was vacuum-distilled using a short-path distillation column, yielding the 1,2-bis(trimethylsiloxy)cycloalkene.

General Procedure for the Synthesis of 1, (*n* + 3)-Bis(trimethylsiloxy)bicyclo[*n* + 1.1.0]alkanes 5.[5,6] A solution of diethylzinc (2.0−2.8 equiv) in toluene (Aldrich, 15 wt % (1.1 M)) was added dropwise over 1 h to a mechanically stirred solution of 1,2-bis(trimethylsiloxy)cycloalkene (**4**) and diiodomethane (2.4−2.7 equiv) (Aldrich, 99%) in dried toluene at 0 °C (ice bath) under a dried N_2 atmosphere. After the addition of the diethylzinc solution was complete, the reaction mixture was stirred at rt for 2−2.5 h. Next, the reaction mixture was slowly poured into 100 mL of cold saturated aqueous NH_4Cl. Quenching the excess diethylzinc in this manner minimized bubbling resulting from the liberation of ethane. The mixture was vacuum-filtered, and the white precipitate was washed with 100 mL of *n*-hexane. The filtered aqueous layer was extracted with the hexane wash from above and was extracted twice more with 100 mL of *n*-hexane. The combined organic layers were washed with 100 mL of saturated aqueous NH_4Cl and 100 mL of saturated aqueous brine. The hexane layer was dried (anhyd Na_2SO_4), and after filtration, the solvent was removed under reduced pressure. The residue was vacuum-distilled using a short-path distillation column to afford the desired compound.

General Procedure for the Synthesis of Cycloalkane-1,3-diones 3.[5,6,7j,15] Anhydrous $FeCl_3$ (4 equiv) (MCB, sublimed, reagent) was quickly transferred to a round-bottom flask under an N_2 atmosphere. Since anhyd $FeCl_3$ dissolves exothermically, the dried DMF was added slowly with mechanical stirring to the ice bath-cooled flask. A solution of the bicycloalkane **5** in dried DMF was added to the stirred mixture, and the reaction was stirred for 3−3.5 h at 60−70 °C. The cooled reaction mixture was poured into 100 mL of cold 10% aqueous HCl, and the mixture was extracted with 100 mL of $CHCl_3$ four times. The combined $CHCl_3$ extracts were washed with 100 mL of 10% aqueous HCl two to three times and then with 100 mL of saturated aqueous brine. The organic layer was dried over anhyd Na_2SO_4 or $MgSO_4$ and suction-filtered and the solvent removed under reduced pressure. If necessary, the residue was reextracted with 50 mL of $CHCl_3$ and 3 × 50 mL of aqueous HCl to remove residual DMF, followed by washing with 50 mL of brine. The $CHCl_3$ solution was dried with anhyd Na_2SO_4 and filtered and the solvent removed under reduced pressure. The crude dione was distilled (bulb-to-bulb) under reduced pressure and then purified by chromatography.

3-Ethoxy-2-cyclohepten-1-one (1, *n* = 3, R = Et). Modifying the procedure of Pirrung and Webster,[6] 15.5 mL (15.5 mmol) of potassium *tert*-butoxide (1.0 M in THF) was added to a solution of 1.56 g (12.4 mmol) of cycloheptane-1,3-dione (**3**, *n* = 3) in 35 mL of dried THF at 0 °C. After the yellow-orange suspension was stirred for 1 h at 0 °C, 20 mL (20 mmol) of triethyloxonium tetrafluoroborate (TEO) (1.0 M in CH_2Cl_2, Aldrich) was added to the reaction. The reaction was stirred for 30 min at 0 °C. The potassium *tert*-butoxide and TEO solutions were added to the reaction a second (8 mmol each) and third (10 mmol each) time to drive the reaction toward completion. The reaction mixture was diluted with 40 mL of diethyl ether and then filtered through a 20 g plug of neutral alumina. The solvents were removed under reduced pressure to give a dark yellow liquid, which was dissolved in 10 mL of ether and filtered through a 5 g plug of neutral alumina. After removal of solvents and purification by flash chromatography (95 CH_2Cl_2/5 ether), the residue was distilled (bulb-to-bulb, 80−100 °C, 5 mmHg) to yield 0.89 g (47%, GC purity 88%) of a colorless liquid: GC−MS *m*/*z* 156, 155, 154 (M^+), 126, 125, 109, 98, 97 (base), 84, 82, 81, 69, 67, 55, 41, 39. Repeated flash chromatography (same conditions) resulted in 0.65 g (34%) of pure product (GC purity 99%): IR (neat) 3450, 3230, 3040, 1625, 1590, 1441, 1368, 1230, 1174 cm^{-1}; ^1H NMR ($CDCl_3$) δ

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(14) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, 1967; pp 1022−1023. preparation of a fine and clean Na sand is critical.

(15) Lewicka-Piekut, S.; Okamura, W. H. *Synth. Commun.* **1980**, *10*, 415.

5.38 (s, 1H), 3.80 (q, J = 7, 2H), 2.59 (m, 4H), 1.84 (m, 4H), 1.34 (t, J = 7, 3H); ^{13}C NMR ($CDCl_3$) δ 202.1, 176.0, 105.7, 64.0, 41.6, 33.0, 23.5, 21.2, 14.1.

The byproduct 2-ethylcycloheptane-1,3-dione (**6**, n = 3, R = Et) was observed by GC−MS: m/z 155, 154 (M^+), 126, 111, 98, 97 (base), 84, 83, 69, 55, 41, 39. The dialkylated byproduct 2-ethyl-3-ethoxy-2-cyclohepten-1-one (**8**, n = 3, R = Et) was observed in the same GC−MS: m/z 184, 183, 182 (M^+, base), 167, 154, 153, 139, 138, 137, 136, 135, 126, 125, 123, 121, 113, 111, 110, 109, 108, 107, 97, 95, 94, 93, 91, 85, 84, 83, 82, 81, 79, 77, 69, 68, 67, 65, 57, 55, 53, 43, 41, 39. It was subsequently isolated from the ensuing flash chromatography in 65% GC purity: ^{1}H NMR ($CDCl_3$) δ 3.98 (q, 2H), 2.55 (m, 4H, partially overlapped by m from starting material **3** present as 9% impurity), 2.31 (q, 2H), 1.78 (m, 4H), 1.34 (t, 3H), 0.95 (t, 3H).

When the 3-ethoxy compound **1** (n = 3) was prepared from 312 mg of **3** (n = 3) using the general procedure for the larger rings (see below), column chromatography (75 CH_2Cl_2/20 n-hexane/5 ether) resulted in 156 mg (41%) of **1** (n = 3) as a colorless liquid: GC purity 99%; TLC (as for column) short wave UV: one trace spot, vanillin: four trace spots, possible on-plate decomposition; UV (n-hexane) λ_{max} 242 nm (ϵ 14 800), 311 nm (ϵ 88).

General Procedure for the Synthesis of the 8-, 9-, and 10-Membered 3-Ethoxy-2-cycloalken-1-ones 1, (n = 4−6, R = Et). Ethyl tosylate was prepared according to the procedure of Fieser and Fieser.[17] This material (2.5 equiv) was added to a stirred solution of potassium *tert*-butoxide (1.1−1.2 equiv, 1.0 M in THF, Aldrich) and the cycloalkane-1,3-dione in dried HMPA under an N_2 atmosphere. The reaction was stirred for 2−3 h at rt and then was extracted with 75 of mL n-hexane and 3 × 50 mL water. To optimize the yields, the aqueous layers were combined and reextracted with 100 mL of n-hexane. This hexane layer was extracted with 3 × 50 mL water, and the hexane layers were combined. After drying (anhyd Na_2SO_4) and filtration, the solvent was removed under reduced pressure, yielding a mixture of product and unreacted ethyl tosylate. Generally, an initial purification was performed by flash chromatography to remove the ethyl tosylate. Subsequent purifications utilized flash chromatography with different solvent systems until a suitably pure material was obtained.

Supporting Information Available: Experimental procedures for specific compounds, spectral data, and Tables 5−8 with details on alkylations of cyclodecane-1,3-dione (**3**, n = 6) (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(16) Schrapler, U.; Ruhlmann, K. *Chem. Ber.* **1964**, *97*, 1383.
(17) Reference 14, p 1180.