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Synthesis of 2,3-Substituted Cycloalkanones by Ceric Ammonium Nitrate-Promoted Oxidative Tandem Additions of 1-Ethoxy-1-[(Trimethylsilyl)oxy]cyclopropane to α,*β*-Unsaturated Cycloalkenones

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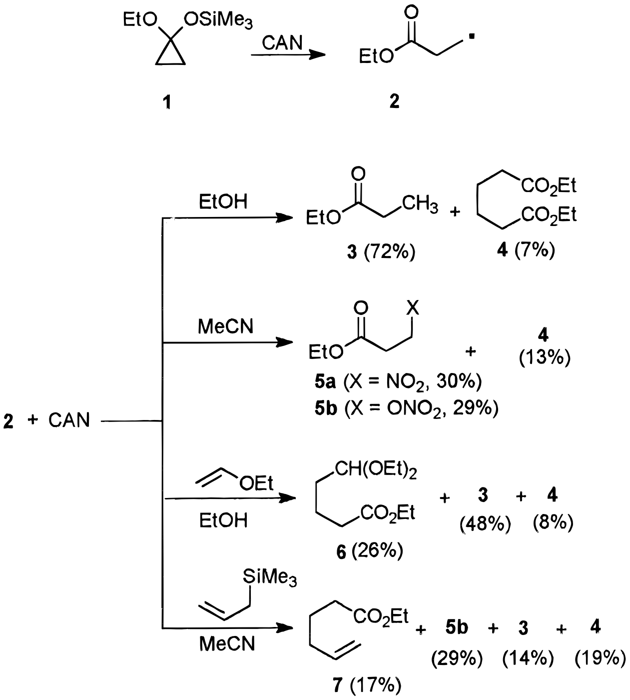
Cyclopropanols and alkoxycyclopropanes are easily oxidized by monoelectronic metal oxidants to generate *β*-carbonylalkyl radicals, which have revealed themselves to be versatile intermediates in carbon−carbon bond formation reactions owing their ability to attack both electron-rich and electron-poor alkenes.[1−3] In the reactions with alkenes bearing an electron-releasing group, a new radical is formed, a nucleophilic species, which undergoes rapid oxidation by the metal to give a highly functionalized product.[2a] On the contrary, the attack at an electron-withdrawing group-substituted alkene generates a hardly oxidizable electrophilic radical which must be trapped in some way in order to avoid extensive polymerization. In this respect, the synthesis reported by Narasaka and coworkers of 1,6-dicarbonyl compounds by manganese(III) 2-pyridinecarboxylate [Mn(pic)$_3$]-promoted addition of [(trialkylsilyl)oxy]cyclopropanes to α,*β*-unsaturated ketones, esters, and nitriles is representative. In this case, the electrophilic adduct radical was trapped by hydrogen abstraction from added tributyltin hydride.[2b]

We recently reported that cerium(IV) ammonium nitrate (CAN) is able to promote a fast oxidative addition of 1-ethoxy-1-(silyloxy)cyclopropane to 1,3-butadienes, affording a mixture of allylic 1,2- and 1,4-nitroxy adducts in good yield and in very mild conditions.[3] To widen the synthetic scope of this process, we replaced the diene by other electron-rich alkenes, such as ethyl vinyl ether and allyltrimethylsilane. However, in these cases, the expected addition products were obtained as minor components among other products derived from the CAN-promoted direct oxidation of the intermediate *β*-(alkoxycarbonyl)alkyl radical (see next section). Owing to the slight nucleophilic character exhibited by the *β*-carbonylalkyl radicals, a certain selectivity in favor of an attack at electron-poor carbon−carbon double bonds with respect to electron-rich ones should be expected. On this basis, we felt it worthwhile to check the possibility of obtaining α,*β*-disubstituted carbonyl compounds by oxidative *tandem* additions of *β*-carbonylalkyl radicals to the corresponding α,*β*-unsaturated precursors in the presence of electron-rich alkenes. In this note, we report on the CAN-promoted addition of 1-ethoxy-1-[(trimethylsilyl)oxy]cyclopropane to 2-cycloalkenones in the presence of ethyl vinyl ether and allyltrimethylsilane, allowing access to highly functionalized regio- and stereoselectively 2,3-disubstituted cycloalkanones.

Scheme 1



Results and Discussion

The reaction of 1-ethoxy-1-[(trimethylsilyl)oxy]cyclopropane (**1**) with CAN (2 equiv) at room temperature is a fast process both in ethanol and in acetonitrile, as evidenced by the rapid decoloration of the mixture (3−4 min). In ethanol, the main reaction product is ethyl propanoate (**3**, 72%, Scheme 1), which forms from the *β*-(ethoxycarbonyl)alkyl radical (**2$^•$**) by hydrogen abstraction from the solvent. Accordingly, an equivalent amount of acetaldehyde diethyl acetal was also detected coming from the fast oxidation of the resulting α-hydroxyethyl radical by CAN.[4] Diethyl adipate (**4**) is also detected (7%), most probably deriving from the dimerization of **2$^•$**. Accordingly, no deuterium incorporation in **4** was observed when the reaction was performed in ethanol-d_6, which excludes the formation of **4** occurring by the attack of **2$^•$** at the ethyl acrylate formed, in turn, from **2$^•$** by an oxidative elimination process.[5] An unidentified product, probably an oligomeric species, has also been detected as a minor component (<5%).

A different pattern of products is observed when acetonitrile is used as the reaction solvent. Here, ethyl 3-nitropropanoate (**5a**, 30%) and ethyl 3-nitroxypropanoate (**5b**, 29%) are formed as the main reaction products, along with **4** (13%) and the above unidentified

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(1) (a) Schaafsma, S. E.; Molenaar, E. J. F.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87,* 1301. (b) Schaafsma, S. E.; Jorritsma, R.; Steinberg, H.; de Boer, Th. J. *Tetrahedron Lett.* **1973**, 827.

(2) (a) Iwasawa, N.; Hayakawa, S.; Isobe, K.; Narasaka, K. *Chem. Lett.* **1991**, 1193. (b) Iwasawa, N.; Hayakawa, S.; Funahashi, M.; Isobe, K.; Narasaka, K. *Bull. Soc. Chim. Jpn* **1993**, *66,* 819.

(3) Belli Paolobelli, A.; Gioacchini, F.; Ruzziconi, R. *Tetrahedron Lett.* **1993**, *34,* 6333.

(4) Rate constants of 10^6−10^8 M^{-1} s^{-1} for oxidation of the 1-hydroxyethyl radical to acetaldehyde by a variety of metals have been reported: Asmus, K.-D.; Bonifacic, M. In *Landolt−Bornstein New Series, Group 2*; Fischer, H., Ed.; Springer Verlag: Berlin, 1984; Vol. 13b, pp 311−313.

(5) This mechanism was suggested by Schaafsma for the oxidation of cyclopropanols by Cu^{2+} and Fe^{3+} salts.[1]

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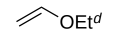
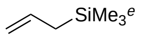
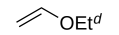
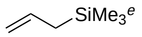
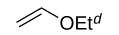
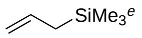
product (<5%). **5a** probably derives from **2**$^\bullet$ by reaction with NO_2 formed in redox processes involving HNO_3 produced in each oxidation step.[6]

The reaction of **1** with CAN in ethanol in the presence of ethyl vinyl ether gives **3** (48%), the expected addition product ethyl 5,5-diethoxypentanoate (**6**) (26%), and **4** (8%). Using a calculated excess of vinyl ethyl ether (3−4 equiv) and considering the reactivity of **2**$^\bullet$ as being similar to that of the ethyl radical in hydrogen abstraction from ethanol ($k = 26$ M^{-1} s^{-1}),[7] a rate constant of 5.3×10^2 M^{-1} s^{-1} for the addition of **2**$^\bullet$ to vinyl ethyl ether can be estimated roughly by means of the competitive method. To test different electron-rich alkenes, we replaced ethyl vinyl ether by allyltrimethylsilane using acetonitrile as the reaction solvent.[9] Once again, the expected ethyl 5-hexenoate addition product **7** was isolated in very low yield (17%), along with **5b** (29%), **4** (19%), and **3** (14%).

The above results betray a substantial nucleophilic character of the β-carbonylalkyl radical, which foreshadows the attack at electron-poor carbon−carbon double bonds occurring faster than both addition to electron-rich carbon−carbon double bonds and hydrogen abstraction from the solvent.[10] In this case, the competitivity of the latter process could be further reduced in favor of the addition process if ethanol is replaced by methanol as the reaction solvent.[11] Indeed, when a mixture of cycloalkenones **8** (Scheme 2), ethyl vinyl ether, and 1-ethoxy-1-[(trimethylsilyl)oxy]cyclopropane was added to a red solution of CAN (~0.5 M) in methanol at room temperature (CAN/**8**/**1**/vinyl ethyl ether 2:1.2:1:6 molar ratio),[12] a fast reaction was observed (5−10 min), and after workup, a crude product was obtained that had spectroscopic characteristics consistent with a mixture of cyclic and acyclic ethyl acetals **9** and **10,** respectively. The acid-catalyzed hydrolysis of the crude mixture in 1:1 chloroform/50% aqueous trifluoroacetic acid gave 2-(formylmethyl)-3-[2-(ethoxycarbonyl)ethyl]cycloalkanones **11**.

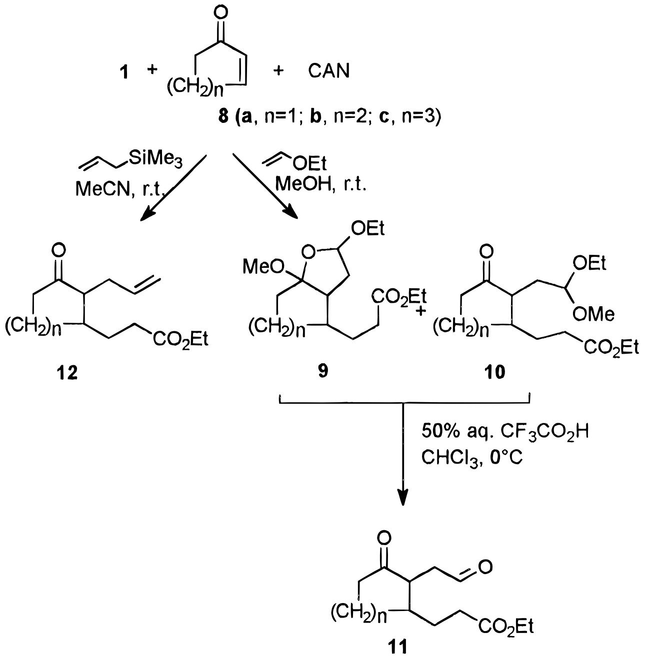
In similar conditions, however, using acetonitrile as the reaction solvent, the oxidative addition of **1** to **8** in the presence of allyltrimethylsilane allowed us to obtain the corresponding 2-allyl-3-[2-(ethoxycarbonyl)ethyl]cycloalkanones **12**. Results are reported in Table 1. Satisfactory yields calculated with respect to the oxidant and in most cases fairly good stereoselectivity were obtained, the *trans*/*cis* ratio ranging from 1.3 to 17, depending on both the ring size and the electron-rich alkene employed, making this procedure competitive, if only for its simplicity, with others based on ionic reactions.[13]

Table 1. Products from CAN-Promoted Oxidative Addition of 1 to the Cycloalkenones 8 in the Presence of Electron-Rich Alkenes

cycloalkenone	electron-rich alkene	product[a]	yield, %[b]	*trans*/*cis*[c] ratio
8a		**11a**	62	17.0
		**12a**	48	6.3
8b		**11b**	42	2.8
		**12b**	31	3.0
8c		**11c**	35	1.3
		**12c**	35	12.0

[a] Mixture of *trans* and *cis* isomers. [b] Isolated yields calculated with respect to CAN. [c] Determined by ^{1}H-NMR and GLC analysis. [d] Solvent, MeOH. [e] Solvent, MeCN.

Scheme 2



The mechanism proposed for the overall process is illustrated in Scheme 3. Oxidation of **1** by CAN generates the β-carbonylalkyl radical **2**$^\bullet$. The fast addition of **2**$^\bullet$ to the β-carbon of the cycloalkenone in turn generates an α-carbonylalkyl radical **13**, now an electrophilic species able to attack the electron-rich carbon−carbon double bond of the vinyl ether or allylsilane before undergoing further oxidation by CAN. The new nucleophilic carbon-centered radical **14** (α-alkoxy or α-(trimethylsilyl)methyl radical) undergoes rapid oxidation to the intermediate carbocation **15**, which, in turn, evolves into a thermodynamic mixture of the acetals **9** and **10**[14] or into the allyl derivative **12**.

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(6) A similar product pattern has been observed in the oxidation of a cyclopentylmethyl radical by CAN in $CH_3COOH/(CH_3CO)_2$: Baciocchi, E.; Belli Paolobelli, A.; Ruzziconi, R. *Tetrahedron* **1992**, *48*, 4617.

(7) The rate constants for the hydrogen abstraction from ethanol by a methyl radical, generating 1-ethoxyethyl radical, are 5.9×10^2 M^{-1} s^{-1} in water at 25 °C and 1.4×10^2 M^{-1} s^{-1} in the gas phase.[8] The ethyl radical has been reported to be less reactive than the methyl radical for the hydrogen abstraction from a $-CH_2-$ group by a factor of 6.7 at 182 °C in the gas phase ($\Delta E_{\mathrm{act.}} = 2.1$ kcal/mol) [Boddy, P. J.; Steacie, E. W. R. *Can. J. Chem.* **1960**, *38*, 1576]. From these data, an extrapolated reactivity ratio Me$^\bullet$/Et$^\bullet$ of ~23 at 25 °C for the hydrogen abstraction from ethanol can be estimated.

(8) Thomas, J. K. *J. Phys.Chem.* **1967**, *71*, 1919

(9) Indeed, acetonitrile proved to be a better solvent than methanol. In the latter solvent, substantial amounts of unidentified byproducts are also formed.

(10) The rate constants of the addition of 5-hexenyl radical to vinyl methyl ketone and methyl acrylate respectively in 3:2 CH_3CN/CH_3COOH at 25 °C are 4.1×10^5 and 2.1×10^5 M^{-1} s^{-1}, respectively [Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674

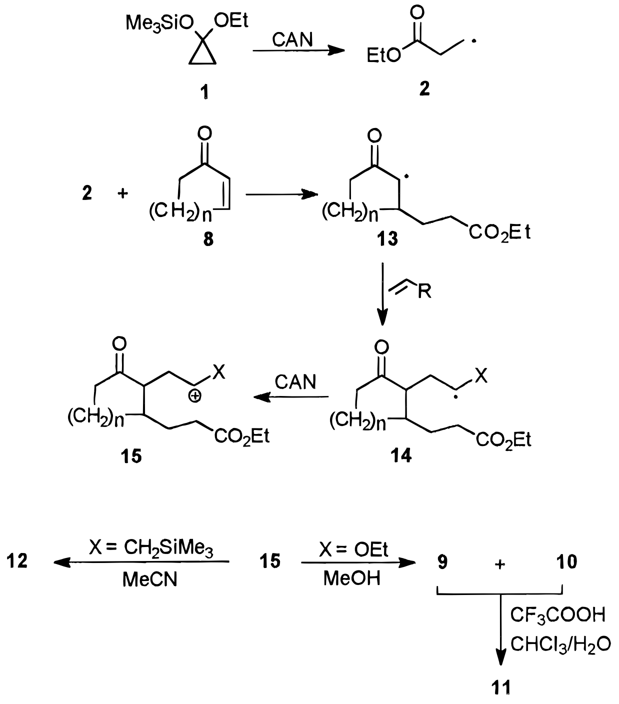
(11) Hydrogen abstraction from methanol by an alkyl radical is ~2.7 times slower than that from ethanol in H_2O at 25 °C.[8]

(12) Powdered calcium carbonate was also added in order to avoid the extensive solvolysis of **1** as well as the acetalization of vinyl ethyl ether catalyzed by the nitric acid produced by CAN in each oxidative process.

(13) For example, a procedure could be envisaged, albeit a rather wearysome one, based on the copper(I)-catalyzed reaction of a zinc homoenolate (see: Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056) with the α,β-unsaturated cycloalkenone, followed by the addition of 2-(bromomethyl)-1,3-dioxolane or allyl bromide as electrophiles.

(14) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Synlett* **1990**, 679.

Scheme 3



Experimental Section

^{1}H- and ^{13}C-NMR spectra were recorded at 200 and 50 MHz, respectively, in CDCl$_3$ in the presence of TMS as internal standard (J values are in hertz). GLC analysis was performed on a 30 m SPB-20 capillary column. Mass spectra were registered at 70 eV.

Reagents and Solvents. Except for ethyl vinyl ether, which was distilled before use, all the organic reagents (Aldrich), of the highest grade of purity, were used as received. Ceric ammonium nitrate (Baker 99%) was dried by heating at 80 °C for 1 h before use. Absolute ethanol, methanol, and acetonitrile (Carlo Erba, ACS grade) were used without further purification.

Oxidation of 1 with CAN in Ethanol. To a red solution of CAN (3.1 g, 5.7 mmol) in 25 mL of ethanol were added powdered calcium carbonate (2.0 g, 20 mmol) and **1** (0.5 g, 2.8 mmol) at room temperature under stirring. The mixture was made to react until complete decoloration (5−6 min), and then it was poured into water (100 mL) and extracted with CH$_2$Cl$_2$ (3 × 20 mL). The collected extracts were washed with water (50 mL) and dried with sodium sulfate. The GLC analysis of the solution showed the presence of substantially two products, which, after solvent evaporation, were identified as ethyl propanoate (**3**, 72%) and diethyl adipate (**4**, 7%) by comparison of their GLC retention times and MS, ^{1}H-NMR, and IR absorptions with those of commercial authentic specimens. A minor product (<5%, probably an oligomeric species) having a much higher GLC retention time was not identified. The same experiment was repeated on a smaller scale (CAN, 125 mg; CaCO$_3$, 80 mg; **1**, 20 mg) using ethanol-d_6 (1 mL) as the solvent. The ^{1}H-NMR and GLC-MS analyses of the reaction mixture showed no deuterium incorporation in **4**.

Oxidation of 1 with CAN in Acetonitrile. The same procedure was used for the oxidation of **1** in acetonitrile. The GLC-MS analysis of the organic extracts allowed to identification of **4** (13%) among two other main products. After solvent evaporation, the latter were isolated by chromatography of the crude mixture on silica gel (8:2 petroleum ether/diethyl ether as the eluent), followed by further purification by HPLC, and identified as ethyl 3-nitropropanoate (**5a**) and ethyl 3-nitroxypropanoate (**5b**) on the base of the following spectroscopic and analytic characteristics. **5a** (30%): ^{1}H-NMR δ 4.74 (t, J = 6.3, 2 H), 4.20 (q, J = 7.1, 2 H), 2.74 (t, J = 6.3, 2 H), 1.28 (t, J = 7.1, 3 H); IR (neat) 2983−2939, 1733, 1559 (ν_{as} NO$_2$), 1374 (ν_{sym} NO$_2$) cm^{-1}; MS m/z (relative intensity) 102 (M$^+$ − OEt, 32), 88 (12), 74 (11), 73 (35), 55 (100), 45 (37). Anal. Calcd for C$_5$H$_9$NO$_4$: C, 40.82; H, 6.16; N, 9.52. Found: C, 40.61; H, 6.54; N, 9.67. **5b** (29%): ^{1}H-NMR δ 4.66 (t, J = 6.1, 2 H), 4.19 (q, J = 7.1, 2 H), 2.97 (t, J = 6.1, 2 H), 1.28 (t, J = 7.1, 3 H); IR (neat) 2985−2935, 1733, 1634 (ν_{as} NO$_2$), 1283 (ν_s NO$_2$); MS m/z (relative intensity) 118 (M$^+$ − OEt, 17), 99 (2), 73 (19), 71 (15), 59 (16), 46 (100). Anal. Calcd for C$_5$H$_9$NO$_5$: C, 36.81; H, 5.56; N, 8.58. Found: C, 36.35; H, 5.81; N, 8.79. A minor component of the mixture (<5%) of high GLC retention time was not identified.

Oxidation of 1 with CAN in the Presence of Ethyl Vinyl Ether. The same procedure described for the oxidation of **1** in ethanol was employed, except that a mixture of ethyl vinyl ether (1.2 g, 17 mmol) and **1** (0.5 g, 2.8 mmol) was added to the red suspension of CAN and powdered CaCO$_3$. After the usual workup, GLC-MS analysis of the organic extracts allowed identification of **3** (48%) and **4** (8%). A third product was isolated by HPLC and identified as ethyl 5,5-diethoxypentanoate (**6**, 26%) on the basis of the following spectroscopic and analytical characteristics: ^{1}H-NMR δ 4.50 (t, J = 5.3, 1 H), 4.12 (q, J = 7.1, 2 H), 3.72−3.41 (m, 16 peaks, 4 H), 2.32 (m, 2 H), 1.67 (m, 4 H), 1.27 (t, J = 7.1, 3 H), 1.19 (t, J = 7.0, 6 H), IR (neat) 2978, 2933, 1735 cm^{-1}; MS m/z (relative intensity) 173 (M$^+$ − OEt, 47), 127 (46), 103 (100), 99 (34), 85 (63), 75 (65), 47 (64). Anal. Calcd for C$_{11}$H$_{22}$O$_4$: C, 60.52; H, 10.16. Found: C, 60.21; H, 9.89.

Oxidative Tandem Addition of 1 to Cycloalkenones 8 in the Presence of Ethyl Vinyl Ether. The procedure described above for the reactions in ethanol was used, except that methanol was employed as the reaction solvent and cycloalkenones **8** (3.4 mmol) were added to reactant mixture. After the usual workup, the crude product, containing a mixture of cyclic (**9**) and acyclic (**10**) acetals (see text), was dissolved in CHCl$_3$ (40 mL) and cooled to 0 °C, and 50% aqueous trifluoroacetic acid (20 mL) was added. After vigorous stirring for 1 h, the mixture was poured into water and extracted with CHCl$_3$ (3 × 20 mL). The organic extracts collected were washed first with water (50 mL) and then with 5% aqueous NaHCO$_3$ and finally dried with Na$_2$SO$_4$. The solvent was evaporated at reduced pressure, and the residual brown oil was chromatographed on silica gel (eluent, 1:1 petroleum ether/diethyl ether) to isolate mixtures of stereoisomeric 2,3-substituted cycloalkanones **11** which were identified on the basis of the following spectral and analytical characteristics.[15]

Ethyl 3-[3-Oxo-2-(2-oxoethyl)cyclopentyl]propanoate (**11a**, 62%). *trans*-**11a**: ^{1}H-NMR δ 9.76 (s, 1 H), 4.12 (q, J = 7.1, 2 H), 2.91−2.65 (8 peaks, AB portion of an ABX system, 2 H), 2.6−2.1 (m, 6 H), 2.1−1.8 (m, 2 H), 1.7−1.4 (m, 2 H), 1.27 (t, J = 7.1, 3 H); ^{13}C-NMR δ 217.5 (C-1), 199.5, 172.8, 60.2, 49.7 (C-2), 41.9, 41.2 (C-3), 36.7, 31.6, 29.2, 26.8, 14.0; IR (neat) 2978, 2931, 2732, 1734, 1588, 1442, 1182, 755 cm^{-1}; MS m/z (relative intensity) 226 (M$^+$, 1), 183 (8), 163 (25), 125 (17), 110 (59), 97 (100), 82 (35), 55 (87). *cis*-**11a**: ^{1}H-NMR absorption of the aldehydic proton δ 9.84; ^{13}C-NMR δ (characterizing peaks) δ 197.0, 51.1, 47.6, 39.3, 34.2, 20.0, 26.7, 24.6; MS m/z (relative intensity) 183 (9), 163 (16), 125 (11), 110 (39), 97 (100), 82 (21), 55 (63). Analysis of the stereoisomeric mixture. Calcd for C$_{12}$H$_{18}$O$_4$: C, 63.70; H, 8.02. Found: C, 63.96; H, 8.19.

Ethyl 3-[3-Oxo-2-(2-oxoethyl)cyclohexyl]propanoate (11b, 42%). *trans*-**11b**: ^{1}H-NMR δ 9.85 (s, 1 H), 4.14 (q, J = 7.1, 2 H), 2.65−1.4 (m, 14 H), 1.25 (t, J = 7.1, 3 H); ^{13}C-NMR δ 209.8 (C-1), 200.5, 172.8, 60.2, 50.3 (C-2), 42.4 (C-3), 40.8, 40.3, 31.0, 30.0, 28.9, 25.2, 13.9; IR (neat) 2935, 2868, 2723, 1727, 1555, 1447, 1420, 1303, 756 cm^{-1}; MS m/z (relative intensity) 195 (M$^+$ − OEt, 4), 177 (16), 139 (21), 124 (53), 111 (100), 110 (60) 97 (42), 55 (83). *cis*-**11b**: ^{1}H-NMR absorption of the aldehydic proton δ 9.78; ^{13}C-NMR (characterizing peaks) δ 200.1, 60.1, 48.5 (C-2), 40.8, 40.3 (C-3), 31.5, 27.2, 21.8; MS m/z (relative intensity) 222 (M$^+$ − H$_2$O, 10), 197 (15), 195 (3), 177 (12), 151 (17), 139 (19), 124 (25), 111(48), 97 (29), 55 (100). Analysis of the isomeric mixture. Calcd for C$_{13}$H$_{20}$O$_4$: C, 64.98; H, 8.39. Found: C, 64.59; H, 8.14.

Ethyl 3-[3-Oxo-2-(2-oxoethyl)cycloheptyl]propanoate (11c, 35%). *trans*-**11c**: ^{1}H-NMR δ 9.76 (s, 1 H), 4.13 (q, J = 7.1, 2 H), 2.61−1.48 (m, 16 H), 1.22 (t, J = 7.1, 3 H); ^{13}C-NMR δ 212.3 (C-1), 200.5, 172.8, 60.1, 48.7 (C-2), 43.7, 43.0, 38.1 (C-3), 32.3, 32.0, 24.1, 23.4, 23.1, 13.9; IR (neat) 2928, 2859, 1728, 1699,

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(15) The products turned brown in the long run at room temperature and upon exposure to the air.

1372, 1179, 732 cm^{-1}; MS m/z (relative intensity) 236 ($M^+ - H_2O$, 90), 191 (78), 165 (49), 153 (89), 125 (100), 95 (47), 55 (83). *cis*-**11c**: ^{1}H-NMR of the aldehydic proton δ 9.77; ^{13}C-NMR δ 212.9 (C-1), 201.3, 172.9, 60.1, 49.0 (C-2), 44.7, 42.3, 38.0, 32.9, 31.3, 30.0, 23.6, 23.0, 13.9. Analysis of the isomeric mixture. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.89; H, 9.01. Olefination of the mixture with 1 equiv of methylenetriphenylphosphorane in THF at 0 °C gave a 1:1.5 mixture of two products, whose GLC retention times and mass spectra were identical to those of **12c** (see below).

Oxidative Addition of 1 to Cycloalkanones 8 in the Presence of Allyltrimethylsilane. The above procedure was used, except that acetonitrile was employed as the reaction solvent. After the usual workup, chromatography of the crude product on silica gel (eluent, 1:1 petroleum ether/diethyl ether) allowed isolation of a mixture of the stereoisomeric 2-allyl-3-[2-(ethoxycarbonyl)ethyl]cycloalkanones **12**, having the following spectroscopic and analytical characteristics.

Ethyl 3-(2-Allyl-3-oxocyclopentyl)propanoate (12a, 48%). *trans*-**12a**: ^{1}H-NMR δ 5.72 (ddt, $J = 17.1, 10.0, 7.1$, 1 H), 4.99 (dq, $J = 17.1, 1.5$, 1 H), 4.95 (dq, $J = 10.0, 1.5$, 1 H), 4.14 (q, $J = 7.1$, 2 H), 2.51−2.25 (m, 5 H), 2.24−1.99 (m, 3 H), 1.98−1.78 (m, 2 H), 1.65−1.30 (m, 2 H), 1.35 (t, $J = 7.1$, 3 H); ^{13}C-NMR δ 218.7 (C-1), 173.0, 135.2, 116.9, 60.2, 54.4 (C-2), 40.5 (C-3), 37.6, 32.2, 31.9, 29.6, 26.6, 14.1; IR (neat) 3076, 2977, 2930, 2873, 1737, 1640, 1442, 1181, 917 cm^{-1}; MS m/z (relative intensity) 224, (M^+, 6), 136 (28), 133 (10), 123 (100), 95 (30), 79 (40), 55 (70). *cis*-**12a**: ^{13}C-NMR (characteristic peaks) δ 116.1, 52.8 (C-2), 38.5, 35.1, 29.1, 24.7, 23.6; MS m/z (relative intensity) 224 (M^+, 4), 151 (14), 136 (25), 123 (100), 95 (58), 79 (78), 67 (60), 55 (69). Analysis of the isomeric mixture. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: 69.42; H, 9.12.

Ethyl 3-(2-Allyl-3-oxocyclohexyl)propanoate (12b, 31%). *trans*-**12b**: ^{1}H-NMR δ 5.88−5.61 (m, 1 H), 5.10−4.97 (m, 2 H), 4.13 (q, $J = 7.2$, 2 H), 2.6−2.1 (br m, 6 H), 2.1−1.8 (br m, 4 H), 1.8−1.5 (br m, 4 H), 1.26 (t, $J = 7.2$, 3 H); ^{13}C-NMR δ 211.5 (C-1), 173.1, 136.2, 116.2, 60.3, 54.9 (C-2), 41.4 (C-3), 40.9, 40.6, 31.6, 28.7, 24.5, 23.6, 14.1; IR (neat) 3073, 3032, 2935, 2869, 2828, 1732, 1707, 1635, 1185, 977, 915 cm^{-1}; MS, 70 eV, m/z (relative intensity) 238 (M^+, 5), 197 (7), 150 (15), 137 (100), 95 (28), 81 (32), 55 (46). *cis*-**12b**: ^{13}C-NMR (characterizing peaks) δ 54.6 (C-2), 40.6 (C-3), 33.6, 32.1, 30.3, 27.3, 25.7, 22.7; MS m/z (relative intensity) 238 (M^+, 7), 197 (18), 151 (26), 137 (100), 95 (43), 81 (50), 55 (70). Analysis of the isomeric mixture. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.30. Found: 70.12; H, 9.58.

Ethyl 3-(2-Allyl-3-oxocycloheptyl)propanoate (12c, 35%). *trans*-**12c**: ^{1}H-NMR δ 5.80−5.57 (m, 1 H), 5.05−4.92 (m, 2 H), 4.12 (t, $J = 7.2$, 2 H), 2.60−2.10 (m, 6 H), 2.00−1.75 (m, 6 H), 1.8−1.5 (m, 4 H), 1.25 (t, $J = 7.2$, 3 H); ^{13}C-NMR δ 214.4 (C-1), 173.3, 135.6, 116.5, 60.3, 58.0 (C-2), 41.6 (C-3), 39.3, 35.3, 31.7, 31.1, 29.0, 27.0, 25.5, 14.2; IR (neat) 3075, 3022, 2931−2863, 1733, 1701, 1640, 1448, 1177, 999, 916 cm^{-1}; MS m/z (relative intensity) 252 (M^+, 7), 206 (17), 178 (20), 151 (82), 95 (62), 81 (85), 55 (100). *cis*-**12c**: ^{13}C-NMR (characterizing peaks) δ 135.6, 116.2, 54.9 (C-2), 43.9 (C-3), 37.7, 35.3, 33.9, 33.0, 30.2, 226.1, 24.4; MS m/z (relative intensity) 252 (M^+, 8), 206 (22), 178 (21), 151 (33), 95 (71), 81 (90), 55 (100). Analysis of the isomeric mixture. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: 70.98; H, 9.73.

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