Ionic Iodocarbocyclization Reactions of 4-Alkenyl- and 4-Alkynylmalonate Derivatives

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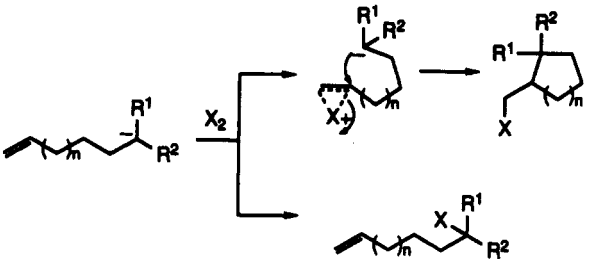
The cyclization reactions of dimethyl 4-alkenylmalonate derivatives **1a–d** in the presence of I_2 and Ti(O*t*-Bu)$_4$ proceed in a highly regio- and stereocontrolled manner (5-exo cyclization and trans addition) to give (iodoalkyl)cyclopentane derivatives **2** or bicyclic lactones **3** through the displacement of the iodide of **2** by an ester group. Iodocarbocyclization reactions of dimethyl [(cycloalkenyl)alkyl]-malonates **1g–i** or dimethyl [(methylenecycloalkyl)alkyl]malonates **1j** and **1k** proceed regio- and stereoselectively to give fused ring compounds or spiro compounds, respectively, as single isomers. Similar reactions of 4-alkynyl derivatives **5** give preferentially *E*-iodomethylene cyclopentane derivatives **6**. An ionic mechanism rather than a radical mechanism is suggested on the basis of the regioselectivity and stereospecificity of the above reactions.

Halocyclization of unsaturated carboxylic acids, alcohols, and amines plays an important role in the synthesis of heterocyclic intermediates and functionalization of double bonds.[1-3] However, the "halocarbocyclization reaction", which involves an intramolecular attack of a carbon nucleophile on a double bond activated by an electrophilic halogenating reagent, has so far been uncommon. The halocarbocyclization reaction should provide a new means for stereoselective construction of functionalized carbocycles because the addition of the carbon nucleophile to an intermediate iodonium ion formed by the reaction of iodine with the multiple bond should proceed in a stereospecific trans manner. A major problem in such a cyclization reaction is that direct halogenation of the carbon nucleophile occurs prior to cyclization (Scheme I).

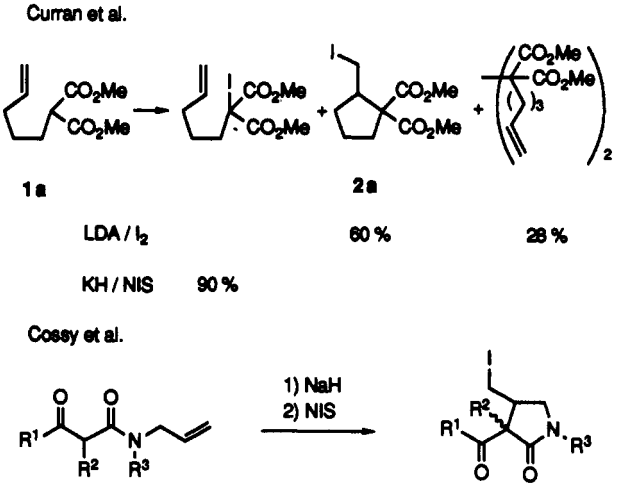
There have been a few reports of cyclization reactions involving the addition of an active methylene compound to a double bond in the presence of a base and an electrophilic iodinating reagent. In the reaction of a 4-pentenylmalonate anion with iodination reagents (LDA and I_2), Curran and his co-worker found that 5-exo cyclized compound **2a** was formed along with the dimeric product (Scheme II).[4] For the mechanism of formation of **2a**, they pointed out the following three possibilities: (1) the cyclization of a free radical that may be formed by oxidation of the anion, (2) normal α-iodination followed by initiation of isomerization by a chain sequence, and (3) an ionic mechanism. Cossy found that treatment of the sodium salt of *N*-allyl β-keto amides with NIS led to the formation of iodomethyl β-keto lactams but proposed no reaction mechanism (Scheme II).[5]

We found that the "iodocarbocyclization reaction" could be performed by treating 4-alkenylmalonates **1** with I_2 and Ti(O*t*-Bu)$_4$.[6,7] Now this iodocarbocyclization reaction

Scheme I



Scheme II



has been extended to acetylenic substrates **5** for the stereoselective synthesis of (iodomethylene)cyclopentanes. The results reported in detail herein indicate that the present reaction, which proceeds by an ionic mechanism involving the intermediacy of an iodonium ion, gives iodocyclopentane derivatives or bicyclic lactones in a highly regio- and stereocontrolled manner under mild conditions. Although radical cyclizations such as iodo atom-transfer reactions[8] and Mn(III)-mediated oxidative cyclizations[9] have been useful for the synthesis of functionalized

(1) (a) Bougalt, M. J. *C. R. Hebd. Seances Acad. Sci.* **1904**, *139*, 864. For recent reviews of halocyclization: (b) Bartlett, P. A.; Richardson, D. P.; Myerson, J. *Tetrahedron* **1984**, *40*, 2371. (c) Gardillo, G.; Orena, M. *Ibid.* **1990**, *46*, 3321.

(2) Enantioselective halocyclization: (a) Fuji, K.; Node, M.; Naniwa, Y.; Kawabata, T. *Tetrahedron Lett.* **1990**, *31*, 3175. (b) Llera, J. M.; Lopez, J. C.; Fraser-Reid, B. *J. Org. Chem.* **1990**, *55*, 2997.

(3) Our recent work on Ti(IV)-mediated stereocontrolled halocyclization: (a) Kitagawa, O.; Sato, T.; Taguchi, T. *Chem. Lett.* **1991**, 177. (b) Kitagawa, O.; Hanano, T.; Tanabe, K.; Shiro, M.; Taguchi, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1005.

(4) Curran, D. P.; Chang, C-T. *J. Org. Chem.* **1989**, *54*, 3140.

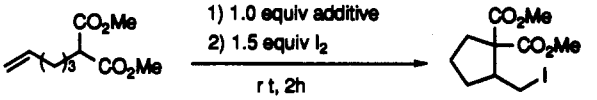
(5) Cossy, J.; Thellend, A. *Tetrahedron Lett.* **1990**, *31*, 1427.

(6) For our preliminary communication of this work: Kitagawa, O.; Inoue, T.; Taguchi, T. *Tetrahedron Lett.* **1992**, *33*, 2167.

(7) Recently, Beckwith has reported that consecutive treatment of allylmalonates with NaH and I_2 affords cyclopentane and cyclopropane derivatives and that the reaction may proceed by an ionic mechanism: Beckwith, A. L. J.; Tozer, M. J. *Tetrahedron Lett.* **1992**, *33*, 4975.

0022-3263/93/1958-3106$04.00/0

Table I. Effect of Additive



1a 2a

entry	additive	solvent	yield (%)
1	Et_3N	CH_2Cl_2	0[a]
2	*s*-collidine	CH_2Cl_2	0[a]
3	BF_3-OEt_2	CH_2Cl_2	0[b]
4	$TiCl_4$	CH_2Cl_2	0[a]
5	*t*-BuOK	THF	31
6	Al(O*t*-Bu)$_3$	C_6H_6	50
7	Zr(O*n*-Bu)$_4$	CH_2Cl_2	22
8	Ti(O*i*-Pr)$_4$	CH_2Cl_2	74
9	Ti(O*t*-Bu)$_4$	CH_2Cl_2	74

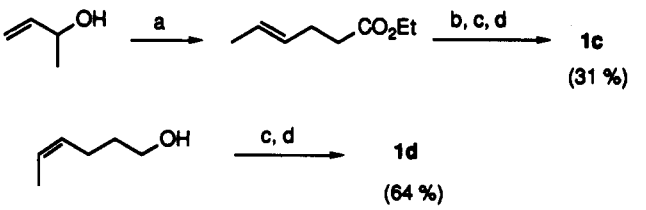
[a] Complex mixture. [b] The product of the addition of I_2 to the olefin is the major product.

carbocycles, these radical approaches have some limitations: the regioselectivity and/or stereospecificity are nonexistent or low when compared to the selectivities of the present reactions. An alternative carbocyclization reaction using similar substrates reported by Gore and his co-workers involves the carbopalladation of a 4-alkenyl- or 4-alkynylmalonate and proceeds by nucleophilic attack on the multiple bond activated by a palladium(II) species. In this reaction, C–C bond formations on both carbon atoms of the multiple bond occur successively by cyclization and coupling of the resultant palladium intermediate with an aryl or vinyl halide.[10]

Results and Discussion

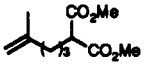
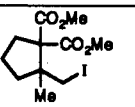
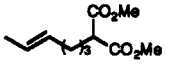
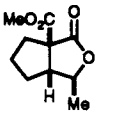
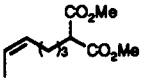
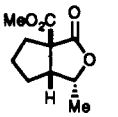
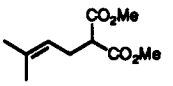
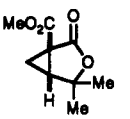
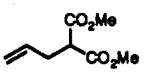
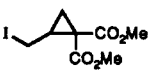
The reaction conditions for cyclization were optimized with dimethyl pentenylmalonate (**1a**) as a substrate. The results of the reactions of **1a** with I_2 in the presence of various additives are summarized in Table I and clearly indicate the effectiveness of metal alkoxide for accomplishing the cyclization reaction (entries 5–9). In particular, titanium alkoxide afforded 5-exo cyclization product **2a** as the sole product in good yield (entries 8, 9). In this case, the corresponding 6-endo cyclization product, the α-iodination product, and the dimer product could not be detected. In the presence of Ti(O*t*-Bu)$_4$, iodination reagents such as NIS and iodonium dicollidine perchlorate[11] and etheral solvents such as THF were not effective for cyclization, and the starting material was recovered in these cases.

Scheme III[a]



[a] Reagents and conditions: (a) 0.05 equiv $EtCO_2H$, $CH_3C(OMe)_3$, 150 °C, 15 h; (b) 2.5 equiv DIBAL, Et_2O, 0 °C; (c) 1.2 equiv MsCl, 1.5 equiv Et_3N, CH_2Cl_2, rt, 2 h; (d) 1.5 equiv NaH, 1.5 equiv $CH_2(CO_2Me)_2$, THF/DMF (5/1), 150 °C, 10 h.

Table II. Iodocarbocyclization Reactions of 4-Alkenylmalonates[a]

entry	substrate	time (h)	product	yield (%)[b]
1	 **1b**	0.5	 **2b**	89
2	 **1c**	13	 **3c (3c/3d = 16.1:1)[c]**	54
3	 **1d**	2	 **3d (3c/3d = 1:48)[c]**	86
4	 **1e**	2	 **3e**	31
5	 **1f**	4	 **2f**	48[d]

[a] Iodocarbocyclization: 1 (0.5 mmol), Ti(O*t*-Bu)$_4$ (0.5 mmol), I_2 (0.75 mmol), CH_2Cl_2 (5 mL), rt. [b] Isolated yield. [c] Determined by 400-MHz ^{1}H-NMR. [d] In this case, pyridine (0.75 mmol) was added.

To investigate the mechanism of the reaction and to compare the reaction with the corresponding radical reaction, we conducted studies with various substrates. Substrates **1c** and **1d** were prepared from commercially available 3-buten-2-ol and *cis*-4-hexen-1-ol,[12] respectively (Scheme III).

The results of the cyclization reactions of **1b–f** in the presence of Ti(O*t*-Bu)$_4$ and I_2 are summarized in Table II. As noted for **1a**,[4] **1b**, which has a methyl group at the internal position of the alkene, gave 5-exo cyclization product **2b** as the only product (entry 1). The cyclization of **1b** is remarkable in contrast with the radical atom-transfer reaction of the corresponding iodomalonate, which exclusively gives the cyclohexane derivative via a 6-endo cyclization (Scheme IV).[4] The differences in the product composition suggest an ionic mechanism rather than a free radical mechanism for the reactions of **1**. Furthermore, the reactions of 4-hexenylmalonates **1c** and **1d** gave bicyclic

(8) Examples of synthesis of functionalized carbocyclic compounds: (a) Curran, D. P.; Chen, M-H.; Kim, D. *J. Am. Chem. Soc.* **1986**, *108*, 2489. (b) Curran, D. P.; Chen, M-H. *Ibid.* **1987**, *109*, 6558. (c) Curran, D. P.; Chen, M-H.; Kim, D. *Ibid.* **1989**, *111*, 6265. (d) Takano, S.; Nisizawa, S.; Akiyama, M.; Ogasawara, K. *Synthesis* **1984**, 949. (e) Mori, M.; Kubo, Y.; Ban, Y. *Tetrahedron* **1988**, *44*, 4321. (f) Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518. (g) Hayes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 5533 and references cited therein.

(9) (a) Heiba, E. I.; Dessau, R. M.; Rodewald, P. G. *J. Am. Chem. Soc.* **1974**, *96*, 7977. (b) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10. (c) Corey, E. J.; Kang, M. *J. Am. Chem. Soc.* **1984**, *106*, 5384. (d) Snider, B. B.; Mohan, R.; Kates, S. A. *J. Org. Chem.* **1985**, *50*, 3659. (e) Dombroski, M. A.; Kates, S. A.; Snider, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 2759. (f) Kates, S. A.; Dombroski, M. A.; Snider, B. B. *J. Org. Chem.* **1990**, *55*, 2427 and references cited therein.

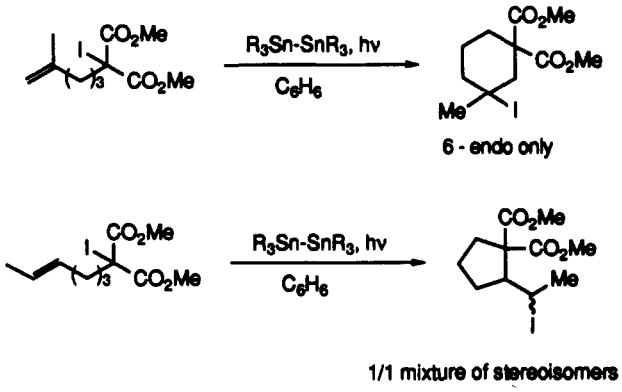
(10) (a) Fournet, G.; Balme, G.; Gore, J. *Tetrahedron Lett.* **1989**, *30*, 69. (b) Fournet, G.; Balme, G.; Gore, J. *Tetrahedron* **1990**, *46*, 7763. (c) Fournet, G.; Balme, G.; Hemelryck, B.; Gore, J. *Tetrahedron Lett.* **1990**, *31*, 5147. (d) Fournet, G.; Balme, G.; Gore, J. *Tetrahedron* **1991**, *47*, 6293. (e) Balme, G.; Bouyssi, D.; Faure, R.; Gore, J.; Hemelryck, B. *Tetrahedron* **1992**, *48*, 3891.

(11) The decomposition of these iodination reagents by Ti(O*t*-Bu)$_4$ may occur faster than the cyclization reaction.

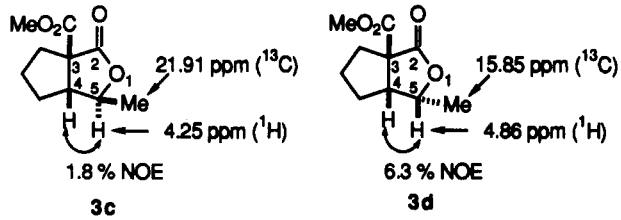
(12) 3-Buten-2-ol and *cis*-4-hexen-1-ol were purchased from Tokyo Kasei Organic Chemicals Co.

Scheme IV

Curran et al.



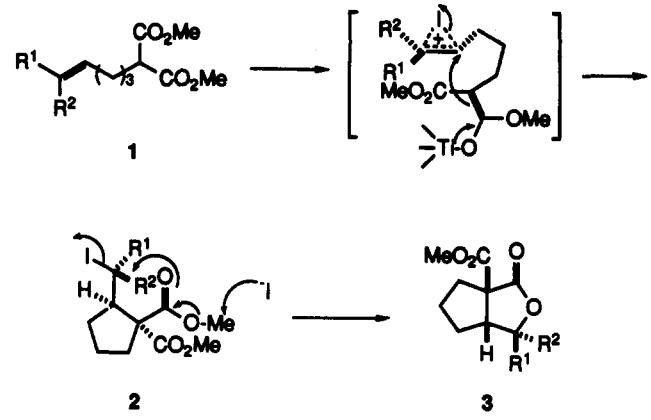
lactones **3c** and **3d**, respectively, through the displacement of the secondary iodide of the cyclization products by an ester group. Lactone **3c** is formed preferentially from *E*-isomer **1c**, and **3d** is formed from *Z*-isomer **1d** (entries 2, 3). The stereochemistry of **3c** was determined to be (4,5)-trans and that of **3d** to be (4,5)-cis. The assignments



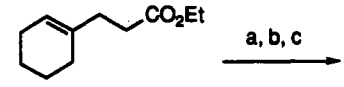
were based on a comparison of the ^1H NMR and ^{13}C NMR spectra of each compound and on NOE experiments. The high stereoselectivity and stereospecificity of the reaction are consistent with an ionic mechanism such as halolactonization and contrast sharply with those of the ditin-mediated radical atom-transfer reaction of the *E*-isomer of 4-hexenyliodomalonate, which gives a 1:1 mixture of diastereomeric iodocyclopentane derivatives (Scheme IV).[4,13] The formation of cyclopropane derivative **3e** from **1e** and that of **2f** from **1f** under reaction conditions similar to those used for **1a–d** may also involve an ionic reaction pathway.[14,15] The yields, however, were lower than those of the cyclopentane derivatives (entries 4, 5).

Attempts to extend the reaction to the production of cyclohexane or cyclobutane derivatives have not yet been successful. For example, 5-alkenyl derivative dimethyl 5-hexenylmalonate and 3-alkenyl derivative dimethyl 3-butenylmalonate gave as the major products dimethyl (5,6-diiodohexyl)malonate and dimethyl (3,4-diiodobutenyl)malonate, respectively, rather than the 6-exo and 4-exo iodocarbocyclization products.[16]

Scheme V



Scheme VI[a]



[a] Reagent and conditions: (a) 2.5 equiv DIBAL, Et_2O, 0 °C, (b) 1.2 equiv MsCl, 1.5 equiv Et_3N, CH_2Cl_2, rt, 2 h; (c) 1.5 equiv NaH, 1.5 equiv $CH_2(CO_2Me)$, THF/DMF (5/2), 150 °C, 10 h.

On the basis of the results discussed above, we believe that the reaction occurs by a 5-exo trans addition of a carbon nucleophile [a Ti(IV) enolate] to a three-membered iodonium ion (Scheme V). If the rate of cyclization is slow, the iodonium ion intermediate is attacked by the iodide instead of the carbon nucleophile, and the formation of the diiodide results. The α-iodination reaction of malonate can be ruled out because α-iodination products of **1a–f** were not detected. In a control experiment, α-iodination of dimethyl benzylmalonate did not take place; only starting material was recovered under the present reaction conditions. When a relatively reactive secondary or tertiary iodide is formed by iodocarbocyclization, the subsequent lactonization occurs with inversion of the configuration of the iodide and leads to product **3**.[17]

Application to Polycyclic Compounds. The use of the present reaction for the synthesis of fused ring systems from cyclic substrates is of particular interest since the reaction would be expected to selectively give products having important structural features found in various natural products. Starting materials **1g** and **1h** were synthesized according to literature procedures.[10e] Compound **1i** was synthesized from ethyl 3-(1-cyclohexenyl)-propionate according to the method outlined in Scheme VI.[18] Compounds **1j** and **1k** were prepared by Salomon's procedure for the ethyl esters.[19]

The results of the reactions of **1g–k** in the presence of I_2 and Ti(O*t*-Bu)$_4$ are summarized in Table III. Cycloalkenyl derivatives **1g** and **1h** gave exclusively cis-fused

(13) Atom-transfer addition reactions of iodomalononitriles to alkenes have been shown to proceed in a nonstereospecific manner: Curran, D. P.; Thoma, G. *Tetrahedron Lett.* **1991**, *32*, 6307.

(14) It is well known that cyclopropylmethyl radical undergoes cleavage of the cyclopropane ring to form a homoallylic radical. The rate constant of the cleavage ($k = 1.3 \times 10^8\ s^{-1}$ at 25 °C) makes the reaction one of the fastest radical reactions, and the equilibrium lies overwhelmingly toward the homoallylic radical. See: (a) de Mayo, P. *Rearrang. Ground Excited States* **1980**, *1*, 227–247. (b) Laurie, D.; Lucas, E.; Nonhebel, D. C.; Suckling, C. J.; Walton, J. C. *Tetrahedron* **1986**, *42*, 1035. (c) Nonhebel, D. C.; Suckling, C. J.; Walton, J. C. *Tetrahedron Lett.* **1982**, *23*, 4477. (d) Suckling, C. J. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 537.

(15) In the reaction of **1f** under the same conditions, ^1H-NMR of the product showed it to be an inseparable mixture of **2f**, starting material, and dimethyl 2,3-diiodopropylmalonate. However, when the reaction of **1f** was carried out in the presence of pyridine, a separable mixture of **2f** and the starting material was obtained without the formation of the diiodide.

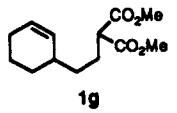
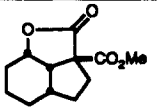
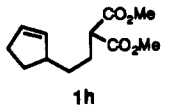
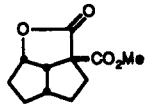
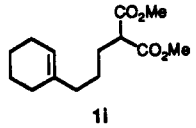
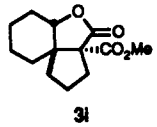
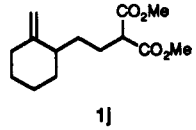
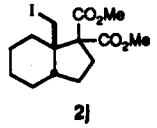
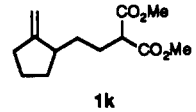
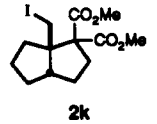
(16) It was reported that, in the presence of PhI, the carbopalladation reaction of dimethyl 5-hexenylmalonate also gave the product of the addition of phenylpalladium iodide to the olefin without the formation of 6-exo cyclization product. See ref 10a.

(17) It is easily anticipated that the resultant HI or (*t*-BuO)$_3$TiI promotes the lactonization reaction.

(18) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 3727.

(19) Salomon, R. G.; Ghosh, S.; Zagorski, M. G.; Reitz, M. *J. Org. Chem.* **1982**, *47*, 829.

Table III. Iodocarbocyclization Reactions of Cyclic Substrates[a]

entry	substrate	time (h)	product	yield (%)[b]
1	 1g	5	 3g	86
2	 1h	4	 3h	65
3	 1i	6	 3i	63
4	 1j	6	 2j	77
5	 1k	6	 2k	60

[a] Iodocarbocyclization: 1 (0.5 mmol), Ti(O*t*-Bu)$_4$ (0.5 mmol), I_2 (0.75 mmol), CH_2Cl_2 (5 mL), rt. [b] Isolated yield.

tricyclic lactones **3g** and **3h**, respectively, through a displacement of the secondary iodide of the 5-exo cyclization product by an ester group (entries 1, 2). This reaction was also effective for the synthesis of a spiro compound: **1i** gave **3i** as the sole product (entry 3). Methylene derivatives **1j** and **1k** gave good yields of cis-fused bicyclo[4.3.0]nonane derivative **2j** and bicyclo[3.3.0]-octane derivative **2k**, respectively (entries 4, 5).

The following results are noteworthy: (1) functionalized bicyclic compounds having multiple chiral centers are formed in a completely regio- and stereocontrolled manner, (2) vicinal quaternary carbons and spiro compounds can be constructed efficiently (entries 3–5), and (3) the regioselective 5-exo cyclizations characteristic of this procedure contrast with the 6-endo cyclizations of the radical reaction (entries 3–5).[8,9]

The stereochemistry of **3g** was determined by comparison of its NMR spectrum with that reported by Curran.[4] The structures of **3h** and **2k** were determined by NOE experiments as shown in Scheme VII. The presence of a cis-fused ring system in **2j** was confirmed on the basis of an NOE experiment on tricyclic lactone **3j** formed by heating **2j**. The structure of **3i** was determined on the basis of analysis of the coupling constants and chemical shifts in the ^{1}H-NMR spectrum of its triacetate **4i**. H_1 of **4i** may be equatorial, since the coupling constant with vicinal hydrogens on the ring is less than 3 Hz. The sterically bulky cyclopentane carbon atom bearing the geminal bis(acetoxymethyl) groups may occupy an equatorial position for the following reasons: (1) the equatorial orientation of the bulky group is thermodynamically favorable and (2) because of the anisotropic effect of the acetoxy group attached to the cyclohexane ring, H_2, which is close to the ring acetoxy group, appears at lower field compared to H_3, H_4, and H_5; the chemical shift difference

Scheme VII

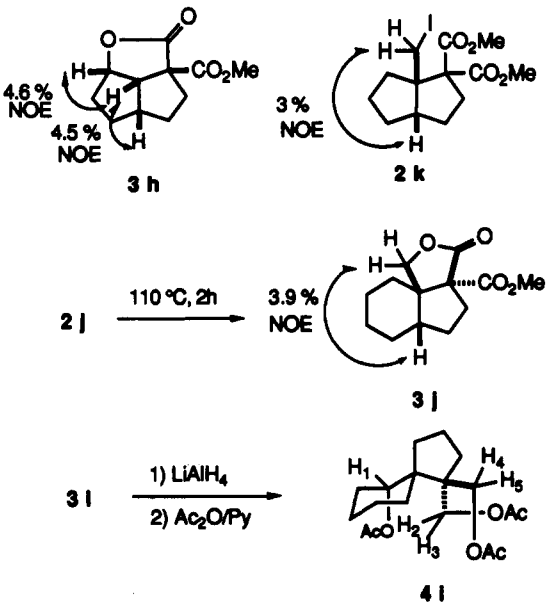
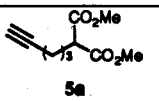
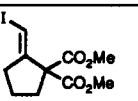
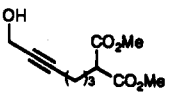
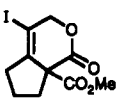
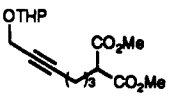
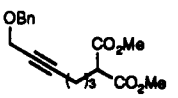
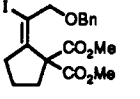
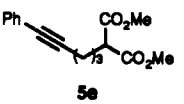
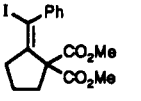


Table IV. Iodocarbocyclization Reactions of 4-Alkynylmalonates[a]

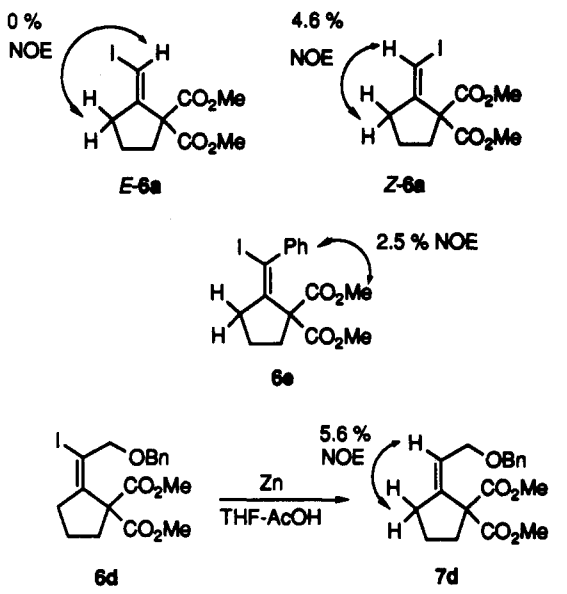
entry	substrate	time (h)	product	yield (%)[b]
1	 5a	0.5	 6a (*E*/*Z* = 28:1)[c]	84
2	 5b	3	 6b	56
3	 5c	0.5	6b	80
4	 5d	0.5	 6d	44
5	 5e	24	 6e	42[d]

[a] Iodocarbocyclization: 5 (0.5 mmol), Ti(O*t*-Bu)$_4$ (0.5 mmol), I_2 (0.6 mmol), CH_2Cl_2 (4 mL), rt. [b] Isolated yield. [c] Determined by 400-MHz ^{1}H-NMR. [d] In this case, pyridine (0.75 mmol) was added.

would not occur if the cyclopentane carbon atom bearing the bis(acetoxymethyl) group was in an axial position on the cyclohexane ring. The regio- and stereochemistry of these products indicate that all reactions proceeded with 5-exo and trans additions and, in particular, the regiochemistry of **3i**, **2j**, and **2k** indicates that they arose from an ionic rather than a radical mechanism.[8,9]

Iodocarbocyclization of 4-Alkynylmalonate. The present reaction is also applicable to 4-alkynylmalonate derivatives **5** to provide iodomethylene cyclopentanes **6** in a highly regio- and stereoselective manner. The results are summarized in Table IV. Starting materials **5a–e** were synthesized according to the procedures reported by Gore

Scheme VIII



et al.[10d] The reaction of 4-pentynylmalonate **5a** gave a good yield of *E*-iodomethylene cyclopentane **6a** in a completely regioselective and highly stereoselective manner (*E*/*Z* = 28). From a disubstituted acetylene such as 4-hexynylmalonate, the product of the addition of I_2 to the alkyne was the major product; no cyclization product was formed. However, the reaction of substituted acetylenes **5b** and **5c**, which have an oxygen function at the terminal position, proceeded smoothly to give bicyclic lactone **6b** as the sole product. Lactonization in the reaction of **5b** and **5c** must have occurred after iodocarbocyclization since, in the absence of I_2, the lactone was not formed when **5b** and **5c** were treated with Ti(O*t*-Bu)$_4$. Similarly to **5b** and **5c**, benzyl ether derivative **5d** also gave cyclization product **6d** as the sole product. 5-Phenyl-4-pentynylmalonate **5e** gave cyclized product **6e** in the presence of pyridine.[20] The stereochemistries of **6a**, **6d**, and **6e** were determined by NOE experiments (Scheme VIII).

Similarly to alkenylmalonate, alkynylmalonates 3-butynyl- and 5-hexynylmalonate gave products of the addition of I_2 to the triple bond as the major products; no iodocarbocyclization products were formed under the same reaction conditions. In the case of propargylmalonate, the formation of methylenecyclopropane was not observed, and a complex mixture was obtained.

Experimental Section

Melting points were determined on a micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400-MHz spectrometer. In ^{1}H and ^{13}C NMR, chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. The mass spectra were recorded by electron impact. Preparative TLC was performed on precoated plates (1 mm thickness, 20 × 20 cm, Merck silica gel 60F-254). Column chromatography was performed on silica gel, Wakogel C-200 (75–150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 × 4 cm i.d. prepacked column (silica gel, 50 μm) with a UV detector.

Starting Materials. All known compounds gave satisfactory physical and spectral data consistent with the literature data. The spectral data of **1c**, **1d**, **1i**, **1j**, and **1k** are given below.

(20) In the absence of pyridine, the product of the addition of iodine to the triple bond was the major product, as it was in the case of **1f**. See ref 15.

(4*E*)-Dimethyl 4-hexenylmalonate (1c): colorless oil; IR (neat) 3010, 2995, 2859, 1739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.42 (1 H, qd, *J* = 5.0, 15.2 Hz), 5.37 (1 H, td, *J* = 7.0, 15.2 Hz), 3.72 (6H, s), 3.35 (1 H, t, *J* = 7.6 Hz), 1.99 (2 H, q, *J* = 7 Hz), 1.89 (2 H, m), 1.63 (3 H, td, *J* = 1.1, 5.0 Hz), 1.36 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 169.7, 130.2, 125.4, 52.2, 51.4, 31.9, 28.2, 27.0, 17.7; MS (*m*/*z*) 215 ($M^+ + H^+$), 183 ($M^+ - OMe$), 182, 154, 152, 151, 145, 132, 122, 95, 81. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.26; H, 8.67.

(4*Z*)-Dimethyl 4-hexenylmalonate (1d): colorless oil; IR (neat) 3014, 2955, 2863, 1737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.46 (1 H, tqd, *J* = 1.3, 6.7, 10.8 Hz), 5.34 (1 H, qtd, *J* = 1.6, 7.2, 10.8 Hz), 3.73 (6 H, s), 3.36 (1 H, t, *J* = 7.6 Hz), 2.06 (2 H, q, *J* = 7.2 Hz), 1.91 (2 H, q, *J* = 7.6 Hz), 1.59 (3 H, dq, *J* = 6.7, 1.6 Hz), 1.37 (2H, tt, *J* = 7.2, 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 169.7, 129.5, 124.4, 52.3, 51.5, 28.3, 27.1, 26.2, 12.6; MS (*m*/*z*) 215 ($M^+ + H^+$), 183 ($M^+ - OMe$), 182, 154, 151, 150, 145, 132, 122, 95, 81. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.42; H, 8.54.

Dimethyl [3-(1-Cyclohexenyl)propyl]malonate (1i): colorless oil; IR (neat) 2997, 2927, 2837, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.38 (1 H, m), 3.73 (6 H, s), 3.36 (1 H, t, *J* = 7.5 Hz), 1.84–1.97 (8 H, m), 1.37–1.61 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 169.9, 136.8, 121.4, 52.3, 51.6, 37.4, 28.4, 28.1, 25.2, 25.2, 22.9, 22.5; MS (*m*/*z*) 255 ($M^+ + H^+$), 254 (M^+), 223, 191, 162, 145, 122. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.73; H, 8.96.

Dimethyl [2-(2-Methylenecyclohexyl)ethyl]malonate (1j): colorless oil; IR (neat) 3069, 2927, 2855, 1757, 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.66 (1 H, s), 4.57 (1 H, s), 3.74 (6 H, s), 3.36 (1 H, t, *J* = 7.5 Hz), 2.20 (1 H, m), 1.98–2.06 (2 H, m), 1.90 (2 H, q, *J* = 7.5 Hz), 1.40–1.78 (6 H, m), 1.23–1.34 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 169.5, 151.6, 105.8, 52.0, 51.5, 42.7, 34.2, 33.5, 29.4, 28.4, 26.7, 23.8; MS (*m*/*z*) 255 ($M^+ + H^+$), 223 ($M^+ - OMe$), 191, 145, 122, 107. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.89; H, 8.76.

Dimethyl [3-(1-Cyclohexenyl)propyl]malonate (1k): colorless oil; IR (neat) 2954, 2875, 1738, 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.87 (1 H, d, *J* = 1.4 Hz), 4.75 (1 H, d, *J* = 1.4 Hz), 3.74 (6 H, s), 3.36 (1 H, t, *J* = 7.5 Hz), 1.48–2.38 (9 H, m), 1.20–1.32 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 169.9, 169.9, 156.0, 104.5, 52.6, 52.4, 51.9, 43.5, 33.1, 32.4, 32.0, 27.1, 24.1; MS (*m*/*z*) 240 (M^+), 222, 209, 191, 177, 159, 145, 133, 108, 93, 79.

General Procedure for Iodocarbocyclization Reactions. To a solution of the malonate (0.5 mmol) in dry CH_2Cl_2 (5 mL) was added Ti(O*t*-Bu)$_4$ (0.2 mL, 0.5 mmol) [in the cases of **1f** and **4e**, pyridine (0.06 mL, 0.75 mmol) was also added]. After the CH_2Cl_2 solution was stirred for 10 min, I_2 (190 mg, 0.75 mmol in the cases of alkenylmalonates **1a–k** and 150 mg, 0.6 mmol in the cases of alkynylmalonates **5a–e**) was added, and then the reaction mixture was stirred at room temperature for the indicated period (see the relevant table). The mixture was poured into 2% HCl and extracted with ether. The ether extracts were washed with aqueous $Na_2S_2O_3$ solution, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by preparative TLC, column chromatography, or MPLC.

Dimethyl 2-(Iodomethyl)cyclopentane-1,1-dicarboxylate (2a). Compound **2a** was prepared from **1a** (100 mg, 0.5 mmol). Purification by preparative TLC (hexane/AcOEt = 5:1) gave **2a** (121 mg, 74%). **2a**: white solid; mp 52–54 °C; IR ($CHCl_3$) 2950, 2875, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.73 (3 H, s), 3.71 (3 H, s), 3.53 (1 H, dd, *J* = 3.4, 9.3 Hz), 2.98 (1 H, dd, *J* = 9.3, 11.3 Hz), 2.86 (1 H, m), 2.47 (1 H, m), 2.12–2.28 (2 H, m), 1.82 (1 H, m), 1.48–1.70 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 171.7, 170.7, 63.0, 52.6, 52.4, 49.3, 35.2, 32.4, 21.7, 6.6; MS (*m*/*z*) 327 ($M^+ + H^+$), 295 ($M^+ - OMe$), 199, 167, 139, 107, 79. Anal. Calcd for $C_{10}H_{15}IO_4$: C, 36.82; H, 4.64. Found: C, 37.19; H, 4.64.

Dimethyl 2-(Iodomethyl)-2-methylcyclopentane-1,1-dicarboxylate (2b). Compound **2b** was prepared from **1b** (107 mg, 0.5 mmol). Purification by preparative TLC (hexane/AcOEt = 5:1) gave **2b** (151 mg, 89%). **2b**: colorless oil; IR ($CHCl_3$) 2945, 2880, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.73 (3 H, s), 3.70 (3 H, s), 3.60 (1 H, d, *J* = 9.5 Hz), 3.58 (1 H, d, *J* = 9.5 Hz), 2.53 (1 H, m), 2.32 (1 H, m), 2.15 (1 H, m), 1.70–1.85 (3 H, m), 1.15 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 171.5, 170.8, 64.7, 52.3, 52.2, 48.5, 39.3, 34.0, 23.8, 18.9, 17.5; MS (*m*/*z*) 341 ($M^+ + H^+$), 340 (M^+), 309, 213, 153, 113, 93. Anal. Calcd for $C_{11}H_{17}IO_4$: C, 38.84; H, 5.04. Found: C, 38.49; H, 5.00.

(3α,3aα,6aα)-Dihydro-3-methyl-6a-carbomethoxycyclopenta[c]furan-1(3H)-one (3c). Compound **3c** was prepared from **1c** (107 mg, 0.5 mmol). Purification by column chromatography (hexane/AcOEt = 8:1) gave a mixture of **3c** and **3d** (54 mg, 54%, **3c**/**3d** = 16.1:1). **3c**: colorless oil; IR ($CHCl_3$) 2950, 2885, 1770, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (1 H, dq, J = 3.7, 6.4 Hz), 3.77 (3 H, s), 2.77 (1 H, td, J = 3.7 and 8.2 Hz), 2.33 (1 H, ddd, J = 6.7, 10.8, 13.4 Hz), 2.25 (1 H, ddd, J = 3.4, 6.7, 13.4 Hz), 1.95 (1 H, m), 1.83 (1 H, m), 1.71 (1 H, m), 1.44 (3 H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 175.8, 171.0, 82.3, 62.6, 53.0, 52.3, 35.4, 33.8, 25.6, 21.9; MS (m/z) 199 ($M^+ + H^+$), 183 ($M^+ - Me$), 167, 154, 139, 126, 111, 95, 79, 67. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.49; H, 7.15.

(3β,3aα,6aα)-Dihydro-3-methyl-6a-carbomethoxycyclopenta[c]furan-1(3H)-one (3d). Compound **3d** was prepared from **1d** (107 mg, 0.5 mmol). Purification by column chromatography (hexane/AcOEt = 8:1) gave a mixture of **3c** and **3d** (86 mg, 86%, **3c**/**3d** = 1:48). **3d**: colorless oil; IR ($CHCl_3$) 2945, 2880, 1765, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (1 H, dq, J = 6.5, 6.5 Hz), 3.76 (3 H, s), 2.93 (1 H, td, J = 6.5, 6.5 Hz), 2.39 (1 H, m), 2.23 (1 H, m), 1.60–1.85 (4 H, m), 1.37 (3 H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 175.9, 170.4, 76.9, 63.7, 52.8, 50.6, 34.2, 27.0, 26.2, 15.89; MS (m/z) 199 ($M^+ + H^+$), 167, 154, 139, 126, 111, 95, 79, 67. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.49; H, 7.11.

(3aα,4aα)-Dihydro-3,3-dimethyl-4a-carbomethoxycyclopropa[c]furan-1(3H)-one (3e). Compound **3e** was prepared from **1e** (200 mg, 1 mmol). Purification by column chromatography (hexane/AcOEt = 5:1) gave **3e** (58 mg, 31%). **3e**: colorless oil; IR ($CHCl_3$) 2945, 2860, 1780, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 2.53 (1 H, dd, J = 5.5, 8.1 Hz), 1.95 (1 H, dd, J = 5.0, 8.1 Hz), 1.51 (3 H, s), 1.44 (1 H, dd, J = 5.0, 5.5 Hz), 1.37 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 169.6, 167.4, 80.9, 52.8, 37.7, 31.5, 29.1, 23.8, 19.9; MS (m/z) 169 ($M^+ - Me$), 153, 127, 91, 84, 74. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.32; H, 6.57.

Dimethyl 2-(Iodomethyl)cyclopropane-1,1-dicarboxylate (2f). Compound **2f** was prepared from **1f** (86 mg, 0.5 mmol). Purification by MPLC (hexane/AcOEt = 20:1) gave **2f** (72 mg, 48%). **2f**: white solid; mp 37 °C; IR (neat) 3005, 2953, 2848, 1723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 3.74 (3 H, s), 3.21 (1 H, dd, J = 7.7, 10.2 Hz), 3.12 (1 H, dd, J = 8.4, 10.2 Hz), 2.47 (1 H, dddd, J = 7.5, 7.7, 8.4, 8.9 Hz), 1.61 (1 H, dd, J = 5.1, 8.9 Hz), 1.52 (1 H, dd, J = 5.1, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 169.3, 167.6, 52.8, 52.7, 38.4, 31.1, 24.1, 1.6; MS (m/z) 298 (M^+), 267, 171, 139, 113, 71. Anal. Calcd for $C_8H_{11}IO_4$: C, 32.23; H, 3.72. Found: C, 32.29; H, 3.60.

(2aα,4aα,7aα,7bα)-Octahydro-2a-carbomethoxyindeno-[7,1-bc]furan-2-one (3g). Compound **3g** was prepared from **1g** (140 mg, 0.58 mmol). Purification by column chromatography (hexane/AcOEt = 8:1) gave **3g** (112 mg, 86%). **3g**: colorless oil; IR (neat) 2941, 2870, 1771, 1743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.81 (1 H, ddd, J = 2.6, 3.3, 6.6 Hz), 3.76 (3 H, s), 2.81 (1 H, dd, J = 6.6, 10.0 Hz), 2.37 (1 H, dd, J = 5.7, 12.7 Hz), 2.20–2.34 (2 H, m), 2.11 (1 H, ddd, J = 6.1, 12.7, 13.6 Hz), 1.65–1.75 (2 H, m), 1.33–1.62 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 176.1, 170.0, 77.1, 64.8, 52.7, 44.6, 36.4, 33.5, 30.2, 27.7, 25.3, 13.2; MS (m/z) 225 ($M^+ + H^+$), 193 ($M^+ - OMe$), 180, 148, 138, 121, 91, 79, 67. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 63.98; H, 7.14.

(2aα,4aα,6aα,6bα)-Octahydro-2a-carbomethoxypentaleno-[6,1-bc]furan-2-one (3h). Compound **3h** was prepared from **1h** (108 mg, 0.48 mmol). Purification by column chromatography (hexane/AcOEt = 8:1) gave **3h** (65 mg, 65%). **3h**: colorless oil; IR (neat) 2958, 2871, 1771, 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.02 (1 H, m), 3.77 (3 H, s), 3.36 (1 H, dd, J = 6.7, 9.3 Hz), 2.74 (1 H, m), 2.55 (1 H, td, J = 7.9, 13.6 Hz), 2.35 (1 H, td, J = 6.7, 13.6 Hz), 2.18 (1 H, m), 2.03 (1 H, dtd, J = 6.0, 7.6, 13.5 Hz), 1.83–1.93 (2 H, m), 1.42–1.57 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 176.3, 170.5, 84.2, 62.4, 57.1, 53.0, 46.1, 35.9, 34.2, 32.2, 29.1; MS (m/z) 211 ($M^+ + H^+$), 179 ($M^+ - OMe$), 166, 151, 138, 125, 107, 91, 79, 67. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.55; H, 6.79.

Spiro Compound 3i. Compound **3i** was prepared from **1i** (127 mg, 0.5 mmol). Purification by column chromatography (hexane/AcOEt = 8:1) gave **3i** (76 mg, 64%). **3i**: colorless oil; IR (neat) 2948, 2872, 1774, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.21 (1 H, dd, J = 5.7, 8.7 Hz), 3.73 (3 H, s), 2.44 (1 H, ddd, J = 7.6, 9.1, 13.5 Hz), 2.25 (1 H, ddd, J = 4.7, 7.3, 13.5 Hz), 1.82–2.01 (4 H, m), 1.55–1.75 (4 H, m), 1.13–1.46 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 176.2, 170.8, 83.5, 64.3, 54.8, 52.5, 42.1, 35.5, 30.8, 28.3, 24.3, 21.0, 20.0; MS (m/z) 239 ($M^+ + H^+$), 207 ($M^+ - OMe$), 194, 178, 162, 150, 135, 93, 91, 79, 67. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.62. Found: C, 65.73; H, 7.48.

(3aα,7aα)-Octahydro-1,1-dicarbomethoxy-7a-(iodomethyl)indene (2j). Compound **2j** was prepared from **1j** (127 mg, 0.5 mmol). Purification by preparative TLC (hexane/AcOEt = 5:1) gave **2j** (146 mg, 77%). **2j**: white solid; mp 65 °C; IR ($CHCl_3$) 2949, 2930, 2870, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.01 (1 H, d, J = 11.5 Hz), 3.75 (1 H, d, J = 11.5 Hz), 3.74 (3 H, s), 3.69 (3 H, s), 2.50 (1 H, m), 2.20–2.33 (2 H, m), 1.73–1.94 (3 H, m), 1.28–1.60 (7 H, m); ^{13}C NMR ($CDCl_3$) δ 171.4, 170.5, 67.0, 52.8, 51.9, 46.7, 42.3, 30.8, 28.8, 24.4, 23.5, 21.4, 19.0, 12.0; MS (m/z) 381 ($M^+ + H^+$), 349 ($M^+ - OMe$), 317, 253, 221, 193, 133, 91, 67. Anal. Calcd for $C_{14}H_{21}O_4$: C, 44.22; H, 5.57. Found: C, 44.52; H, 5.57.

(3aα,6aα)-Octahydro-1,1-dicarbomethoxy-6a-(iodomethyl)pentalene (2k). Compound **2k** was prepared from **1k** (120 mg, 0.5 mmol). Purification by preparative TLC (hexane/AcOEt = 5:1) gave **2k** (111 mg, 60%). **2k**: colorless oil; IR (neat) 2953, 2871, 1773, 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.89 (1 H, d, J = 10 Hz), 3.73 (3 H, s), 3.71 (3 H, s), 3.71 (1 H, d, J = 10 Hz), 2.61 (1 H, m), 2.08–2.35 (4 H, m), 1.75–1.93 (2 H, m), 1.65 (1 H, m), 1.37–1.53 (2 H, m), 1.33 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 171.4, 171.3, 68.2, 58.7, 52.5, 52.2, 50.8, 37.9, 34.9, 34.7, 30.7, 25.6, 16.6; MS (m/z) 367 ($M^+ + H^+$), 335 ($M^+ - OMe$), 303, 275, 239, 207, 179, 147, 119, 91, 67. High-resolution MS calcd for $C_{12}H_{16}O_3I$ ($M^+ - OMe$) 335.01442. Found 335.01382.

(3aβ,5aα,9aα)-Octahydro-3-dicarbomethoxyindeno[7a,1-c]furan-3(1H)-one (3j). After **2j** (114 mg, 0.3 mmol) was heated at 140 °C for 5 h, purification by column chromatography (hexane/AcOEt = 6:1) gave **3j** (64 mg, 90%). **3j**: white solid; mp 52–53 °C; IR ($CHCl_3$) 2932, 2860, 1775, 1741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.33 (1 H, d, J = 8.8 Hz), 4.10 (1 H, d, J = 8.8 Hz), 3.74 (3 H, s), 2.68 (1 H, ddd, J = 2.1, 9.5, 14.5 Hz), 2.15 (1 H, ddd, J = 8.9, 9.0, 14.5 Hz), 1.85–2.03 (2 H, m), 1.48–1.75 (6 H, m), 1.27–1.41 (2 H, m), 1.06 (1 H, tq, J = 3.3, 13.3 Hz); ^{13}C NMR ($CDCl_3$) δ 177.6, 169.0, 74.7, 65.3, 53.8, 52.5, 43.1, 29.6, 28.0, 26.5, 24.1, 22.7, 20.2; MS (m/z) 239 ($M^+ + H^+$), 238 (M^+), 207, 194, 178, 162, 151, 135, 119, 105, 91, 79, 67. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.62. Found: C, 65.18; H, 7.60.

1,1-Bis(acetoxymethyl)-6-acetoxyspiro[4.5]decene (4i). To a suspension of $LiAlH_4$ (8 mg, 0.2 mmol) in THF (1 mL) at rt was added a THF solution (1 mL) of **3c** (24 mg, 0.1 mmol), and then the mixture was refluxed for 2 h. To the mixture were added successively AcOEt, MeOH, and 2% HCl, and then the mixture was extracted with ether. The ether extracts were dried over $MgSO_4$ and evaporated to dryness. To the residue were added CH_2Cl_2 (2 mL), pyridine (0.3 mL), Ac_2O (0.2 mL), and *N,N*-dimethyl-4-aminopyridine (3 mg), and then the mixture was stirred for 15 h at rt. The mixture was poured into 2% HCl and extracted with ether. The extracts were washed with aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 3:1) gave **4i** (8 mg, 23%). **4i**: white solid; mp 83 °C; IR ($CHCl_3$) 2942, 2880, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (1 H, m), 4.57 (1 H, d, J = 11 Hz), 4.11 (1 H, d, J = 11 Hz), 4.06 (1 H, d, J = 11.9 Hz), 3.99 (1 H, d, J = 11.9 Hz), 2.12 (3 H, s), 2.01 (3 H, s), 1.99 (1 H, s), 1.20–2.08 (14 H, m); MS (m/z) 340 (M^+), 281, 280, 220, 178, 161. High-resolution MS calcd for $C_{18}H_{28}O_6$ (M^+) 340.1886. Found 340.1894.

(*E*)- and (*Z*)-1,1-Dicarbomethoxy-2-(iodomethylene)cyclopentane (6a). Compound **6a** was prepared from **5a** (128 mg, 0.65 mmol). Purification by MPLC (hexane/AcOEt = 20:1) gave (*E*)-**6a** (169 mg, 81%) and (*Z*)-**6a** (6 mg, 3%). (*E*)-**6a**: white solid; mp 30 °C; IR ($CHCl_3$) 2953, 1734, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.59 (1 H, t, J = 2.6 Hz), 3.74 (6 H, s), 2.49 (2 H, t, J = 7.2 Hz), 2.44 (2 H, dt, J = 2.6, 7.2 Hz), 1.80 (2 H, quint, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 169.8, 149.9, 78.6, 65.0, 53.0, 37.9, 37.5, 23.0; MS (m/z) 324 (M^+), 293, 265, 197, 169, 138, 123, 77. Anal. Calcd for $C_{10}H_{13}IO_4$: C, 37.05; H, 4.04. Found: C, 37.40; H, 3.94. (*Z*)-**6a**: ^1H NMR ($CDCl_3$) δ 6.46 (1 H, t, J = 2.0 Hz), 3.79 (6 H, s), 2.56 (2 H, dt, J = 2.0, 7.3 Hz), 2.48 (2 H, t, J = 6.8 Hz), 1.80 (2 H, quint, J = 7.1 Hz).

4-Iodo-7a-carbomethoxycyclopenta[c]pyran-1(3H)-one (6b). Compound **6b** was prepared from **5c** (156 mg, 0.5 mmol).

Purification by column chromatography (hexane/AcOEt = 8:1) gave **6b** (129 mg, 80%). **6b**: white solid; mp 63 °C; IR ($CHCl_3$) 2960, 2880, 1756, 1738, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.13 (1 H, td, J = 3.1, 15.4 Hz), 4.82 (1 H, td, J = 1.4, 15.4 Hz), 3.76 (3 H, s), 2.73 (1 H, ddd, J = 3.1, 7.3, 13.4 Hz), 2.39–2.60 (2 H, m), 2.24 (1 H, ddd, J = 8.5, 10.2, 13.4 Hz), 2.08 (1 H, m), 1.85 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 167.9, 167.8, 147.1, 83.0, 76.2, 61.4, 53.3, 35.2, 34.9, 21.5; MS (m/z) 322 (M^+), 263, 195, 167, 151, 136, 108, 91, 65. Anal. Calcd for $C_{10}H_{11}IO_4$: C, 37.29; H, 3.44. Found: C, 37.40; H, 3.43.

(*E*)-1,1-Dicarbomethoxy-2-[iodo[(benzyloxy)methyl]methylidene]cyclopentane (6d). Compound **6d** was prepared from **5d** (159 mg, 0.5 mmol). Purification by MPLC (hexane/AcOEt = 20:1) gave **6d** (96 mg, 44%). **6d**: colorless oil; IR (neat) 2952, 2850, 2800, 1726, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26–7.44 (5 H, m), 4.67 (2 H, s), 4.16 (2 H, t, J = 1.4 Hz), 3.71 (6 H, s), 2.61 (2 H, tt, J = 1.4, 7.4 Hz), 2.55 (2 H, t, J = 6.8 Hz), 1.77 (2 H, tt, J = 6.8, 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3, 146.6, 138.2, 128.3, 127.9, 105.6, 74.3, 72.0, 64.0, 53.0, 43.5, 40.4, 23.6; MS (m/z) 353 (M^+ – Bn), 317, 293, 257, 225, 197, 152, 119. Anal. Calcd for $C_{18}H_{21}IO_5$: C, 48.66; H, 4.77. Found: C, 48.55; H, 4.51.

(*E*)-1,1-Dicarbomethoxy-2-[iodo(phenyl)methylidene]cyclopentane (6e). Compound **6e** was prepared from **5e** (137 mg, 0.5 mmol). Purification by MPLC (hexane/AcOEt = 30:1) gave **6e** (85 mg, 42%). **6e**: white solid; mp 92 °C; IR (KBr) 2986, 2952, 2914, 2879, 2837, 1751, 1729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17–7.45 (5 H, m), 3.39 (6 H, s), 2.67 (2 H, t, J = 7.5 Hz), 2.56 (2 H, t, J = 6.9 Hz), 1.73 (2 H, tt, J = 6.9, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 170.0, 146.3, 143.1, 128.9, 127.9, 127.6, 98.2, 65.0, 52.5, 42.9, 40.9, 22.8; MS (m/z) 400 (M^+), 369, 310, 273, 245, 214, 185, 154, 128. Anal. Calcd for $C_{16}H_{17}IO_4$: C, 48.02; H, 4.28. Found: C, 48.21; H, 4.15.

(*Z*)-1,1-Dicarbomethoxy-2-[[(benzyloxy)methyl]methylidene]cyclopentane (7d). To a solution of **6d** (84 mg, 0.19 mmol) in THF/AcOH (3 mL/1 mL) at rt was added Zn dust (25 mg, 0.38 mmol), and then the reaction mixture was stirred at 80 °C for 6 h. The mixture was poured into 2% HCl and extracted with ether. The ether extracts were washed with aqueous NaCl solution, dried over $MgSO_4$, and evaporated to dryness. Purification by MPLC (hexane/AcOEt = 20:1) of the residue gave **7d** (37 mg, 58%). **7d**: colorless oil; IR (neat) 3030, 2953, 2845, 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–7.35 (5 H, m), 5.84 (1 H, tt, J = 2.1, 6.7 Hz), 4.48 (2 H, s), 4.08 (2 H, dt, J = 1.7, 6.7 Hz), 3.69 (6 H, s), 2.49 (2 H, tq, J = 1.8, 7.3 Hz), 2.37 (2 H, t, J = 6.8 Hz), 1.74 (2 H, tt, J = 6.8, 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 171.3, 141.3, 138.6, 128.3, 127.7, 127.5, 125.8, 72.5, 68.1, 62.4, 52.7, 52.4, 38.6, 35.2, 24.4; MS (m/z) 318 (M^+), 258, 241, 227, 212, 195, 167, 135, 91. Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.84; H, 7.14.