Intramolecular Cooperative Reactions of 1,2-Bis(diazoketone)s. The First Syntheses of *trans*-Hydro-1*H*-2-inden-1-ones

Kazuhiko Nakatani,*[1] Kazunori Takada, and Sachihiko Isoe

Institute of Organic Chemistry, Faculty of Science, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi, Osaka 558, Japan

Received December 14, 1994[⊗]

The intramolecular cooperative reactions of 1,2-bis(diazoketone)s initiated by the Wolff rearrangement of α-diazoketones have been investigated. Under thermal conditions, 1,2-bis(diazoketone)s are efficiently transformed into 2-cyclopenten-1-one derivatives with complete stereospecificity. Thus, a most extraordinary result is reported, that *trans*-hydro-2-inden-1-ones (**1**–**3**) were synthesized for the first time from *trans*-1,2-bis(diazoketone)s (**5**, **11**, and **12**), respectively. The unprecedented *trans*-hydroindenone structure was confirmed by X-ray analysis of **3** as well as ^{1}H NMR analysis and was supported by *ab initio* molecular orbital calculations. The same reactions were also carried out under photochemical conditions and were applied to 1,3-bis(diazoketone)s, giving 2-cyclohexen-1-one derivatives.

Introduction

While the Wolff rearrangement of α-diazoketones is frequently used for the homologation of carboxylic acids and for ring contractions,[2,3] other synthetic applications have been limited.[4,5] This is because a nucleophile to trap the resulting reactive ketene should be present in the reaction medium in order to achieve an efficient reaction. In the presence of protic nucleophiles such as water, alcohols, and amines, such reactions would produce carboxylic acid derivatives. Nonetheless, the Wolff rearrangement, in the absence of protic nucleophiles, has been extensively studied in searching for other synthetic uses of α-diazoketones.[6] Under such conditions, the ketenes produced are trapped with unreacted α-diazoketone.[7–9] Although these intermolecular cooperative reactions are mechanistically interesting, they have not drawn much attention due to the inherent difficulties in controlling the reactions. Unlike these intermolecular reactions, intramolecular cooperative reactions of α-diazoketones are expected to undergo much more specific reactions because of the restricted orientation of the two reactive functionalities.

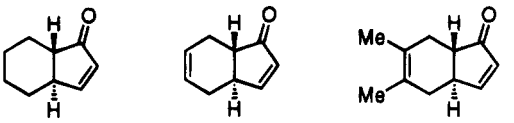


Figure 1. *trans*-Hydroindenones synthesized in these studies.

We recently reported on the syntheses and intramolecular cooperative reactions of 1,2-bis(diazoketone)s, having found that their thermal reactions afforded 4- and 5-substituted 2-cyclopenten-1-one derivatives.[10] The most extraordinary result of this study was that the unprecedented *trans*-hydro-2-inden-1-ones (**1**–**3**) (Figure 1), without substituents at the ring junctions, were obtained in excellent yields. Although these *trans*-hydroindenone structures are quite simple, they have never been synthesized by conventional synthetic methods. The thermal reaction of 1,2-bis(diazoketone)s is an indispensable method for the synthesis of various 2-cyclopenten-1-one derivatives and significantly expands the utility of α-diazoketones.

Results and Discussions

Synthesis of 1,2-Bis(diazoketone)s. Although 1,1- and 1,3-bis(diazoketone)s have been synthesized by the conventional method utilizing the reaction of diazomethane with acid chlorides,[11,12] it was reported that the application of this method to the preparation of 1,2-bis(diazoketone)s is complicated.[11–13] Due to these difficulties, reactions of 1,2-bis(diazoketone)s have been little studied. We first focused our attention on the synthesis of 1,2-bis(diazoketone)s, especially those incorporated in ring systems, because they might provide suitable conformations for the intramolecular reaction of two diazoketone moieties.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1995.

(1) Present address: Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan.

(2) Gill, G. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, pp 887–912.

(3) Meier, H.; Zeller, K.-P. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 32–43.

(4) For the vinylogous Wolff rearrangement, see: (a) Smith, A. B., III; Toder, B. H.; Richmond, R. E.; Branca, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3995. (b) Smith, A. B., III; Toder, B. H.; Richmond, R. E.; Branca, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4001.

(5) For the references of other synthetic utilities of α-diazoketones, see: (a) acid-promoted decomposition; Smith, A. B., III; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407–2439. (b) Reactions of carbonyl ylides: Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22–28. (c) Rh^{II} catalyzed reactions: Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765–1808.

(6) Recent examples, see: (a) Padwa, A.; Austin, D. J.; Chiacchio, U.; Kassir, J. M.; Rescifina, A.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 5923–5926. (b) Padwa, A; Chiacchio, U.; Fairfax, D. J.; Kassir, J. M.; Litrico, A.; Semones, M. A., Xu, S. L. *J. Org. Chem.* **1993**, *58*, 6429–6437. (c) Nakatani, K.; Isoe, S.; Maekawa, S.; Saito, I. *Tetrahedron Lett.* **1994**, *35*, 605–608.

(7) Takebayashi, M.; Ibata, T. *Bull. Chem. Soc. Jap.* **1968**, *41*, 1700–1707.

(8) Wiberg, K. B.; Hutton, J. W. *J. Am. Chem. Soc.* **1954**, *76*, 5367–5371.

(9) Yates, P.; Clark, T. J. *Tetrahedron Lett.* **1961**, 435–439 and also references in refs 2 and 3.

(10) Nakatani, K.; Takada, K.; Odagaki, Y.; Isoe, S. *J. Chem Soc., Chem. Commun.* **1993**, 556–557.

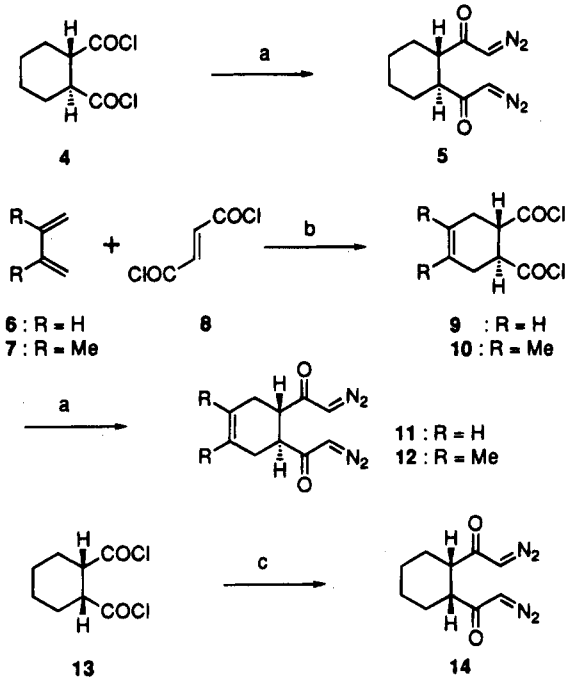
(11) Yates, P.; Dewey, R. S. *Chem. Ind. (London)* **1960**, 749–750.

(12) (a) Font, J.; Serratosa, F.; Valls, J. *J. Chem. Soc., Chem. Commun.* **1970**, 721–722. (b) Font, J.; Valls, J.; Serratosa, F. *Tetrahedron* **1974**, *30*, 455–458.

(13) Fahr, E. *Liebigs Ann. Chem.* **1960**, *638*, 1–32 and see also ref 11.

0022-3263/95/1960-2466$09.00/0

Scheme 1[a]



[a] Reagents: (a) CH_2N_2, **5** (48%), **11** (34%), **12** (21%); (b) rt, overnight for **9** (93%), rt, 48 h for **10** (76%); (c) $LiC(N_2)SiPhMe_2$, **14** (27%).

In contrast to the predicted complexity, it was found that *trans*-1,2-bis(diazoketone) **5** was easily synthesized from *trans*-cyclohexane-1,2-dicarboxylic acid via the reaction of diacid chloride **4**[14] with diazomethane (Scheme 1). The Diels–Alder reaction of butadiene (**6**) or 2,3-dimethylbutadiene (**7**) with fumaryl chloride (**8**), followed by reaction with diazomethane, was an efficient method for the preparation of *trans*-bis(diazoketone)s **11** and **12**, respectively. On the other hand, the synthesis of *cis*-1,2-bis(diazoketone) **14** from *cis*-diacid chloride **13**[15,16] was difficult; no detectable product was obtained by reaction with diazomethane. After much experimentation, we found that the lithium salt of (trimethylsilyl)diazomethane[17] or (dimethylphenylsilyl)diazomethane,[18] in lieu of diazomethane, produced **14** in a modest but acceptable yield.[19] With 1,2-bis(diazoketone)s in hand, we examined their Wolff rearrangements under thermal and photochemical conditions. To prevent any undesirable intermolecular reactions,[8,9,20] and to achieve efficient intramolecular cooperative reactions, all bis(diazoketone) reactions we describe herein were conducted in aprotic medium under dilute conditions.

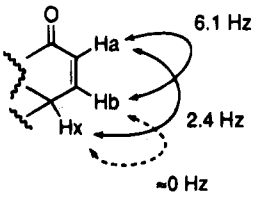
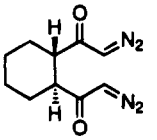
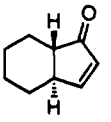
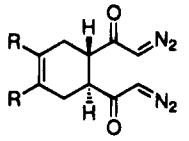
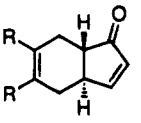
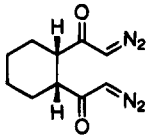
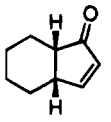


Figure 2. Coupling pattern in ^1H NMR of *trans*-hydroindenone **1**.

Table 1. Thermal Cyclization of Cyclic 1,2-Bis(diazoketone)s

bis(diazoketone)s	product	yield (%)
		
5	**1**	92[a]
		
11 : R = H **12** : R = Me	**2** : R = H **3** : R = Me	85[b] 53[a]
		
14	**15**	72[c]

[a] Reaction was carried out in refluxing toluene. [b] In benzene at 170 °C. [c] In toluene at 170 °C. The reaction at 170 °C was done in a sealed tube.

Thermal Reactions of Cyclic 1,2-Bis(diazoketone)s in Aprotic Medium. When *trans*-1,2-bis(diazoketone) **5** was heated in refluxing toluene, a single product **1** was obtained in high yield. The molecular formula was determined to be $C_9H_{12}O$ by its high resolution mass spectrum (HRMS). The ^1H NMR spectrum of **1** indicated the characteristic coupling pattern of two vinyl hydrogens involved in a typical α,β-unsaturated carbonyl functionality. Thus, the vinyl hydrogen (Ha) at the α position to the carbonyl group was observed at 6.03 ppm as a doublet of a doublet (J = 6.1, 2.4 Hz), while the other vinyl hydrogen (Hb) (β to the carbonyl) was observed at 7.46 ppm as a slightly broadened doublet (J = 6.1 Hz). The allylic hydrogen (Hx) had a typical allylic coupling with Ha (2.4 Hz), but the vicinal coupling with Hb was too small to be measured (Figure 2). One possible interpretation of these NMR data is that the dihedral angle of Hb–C–C–Hx is close to 90°. By considering the molecular formula of **1**, it was identified to be the unprecedented *trans*-3a,4,5,6,7,7a-hexahydro-1*H*-inden-1-one (Table 1). Molecular orbital calculations of **1** indicated that the dihedral angle of Hb–C–C–Hx (now 3-H–C_3–C_{3a}–3a-H) in the optimized geometry at the 3-21G(*) level is 83.7°,[21] which is in good agreement with the angle estimated from the coupling constant observed in the ^1H NMR spectrum. The structure of the

(14) Fuson, R. C.; Speck, S. B.; Hatchard, W. R. *J. Org. Chem.* **1945**, *10*, 55–61.
(15) Ives, D. J.; Sames, K. *J. Chem. Soc.* **1943**, 513–517.
(16) While we have succeeded to get *cis*-1,2-bis(diazoketone) **14** from **13** prepared from the corresponding *cis*-diacid with PCl_5, ^{13}C NMR of **13** unexpectedly indicated a mixture of **13** and **4**, with **4** being a major component. Since we could not detect *trans*-isomer **5** in the synthesis of **14** from **13**, it seemed that **13** rapidly isomerized to **4** in solvents at ambient temperature. Ives and Sames also could not isolate **13**.[15]
(17) (a) Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1982**, *30*, 3450–3452. (b) Aoyama, T.; Sudo, K.; Shioiri, T. *Chem. Pharm. Bull.* **1982**, *30*, 3849–3851. (c) Aoyama, T.; Shioiri, T. *Tetrahedron Lett.* **1986**, *27*, 2005–2006. See also (d) Aoyama, T.; Shioiri, T. *Tetrahedron Lett.* **1980**, *21*, 4461–4462. (e) Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1981**, *29*, 3249–3255.
(18) Shioiri, T.; Aoyama, T.; Mori, S. *Org. Synth.* **1990**, *68*, 1–7.
(19) The yield-decreasing process in the synthesis of **14** could be some intramolecular reactions between the unreacted acid chloride and the produced diazoketone functionality.
(20) (a) Yates, P. *J. Am. Chem. Soc.* **1952**, *74*, 5376–5381. (b) Serratosa, F.; Quintana, J. *Tetrahedron Lett.* **1967**, 2245–2249. (c) Quintana, J.; Torres, M.; Serratosa, F. *Tetrahedron* **1973**, *29*, 2065–2076.

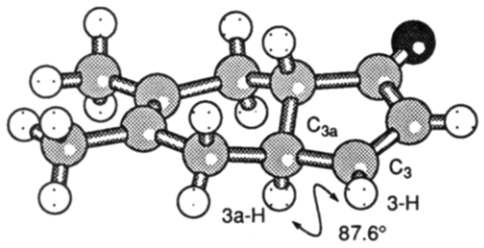
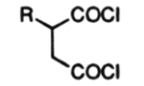
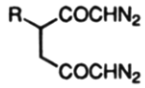
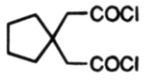
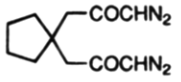
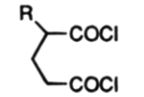
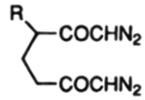


Figure 3. X-ray structure of **3**.

trans-hydroindenone system was proved by X-ray analysis of *trans*-tetrahydroindenone **3** (Figure 3).[36] Thus, the thermal reaction of **12** in refluxing toluene afforded the enone **3**, which crystallized from hexane after silica gel chromatography. The ^1H and ^{13}C NMR spectra of the enone portion of **3** were very much like those of **1**, with the dihedral angle for 3-H−C_3−C_{3a}−3a-H in the crystal structure determined to be 87.6°.[22] These experimental determinations justified our NMR assignment of **1** and validated the calculations. The thermal reaction of **5** can be accomplished using various aprotic solvents at their boiling points, with the yield of **1** increasing as the reaction temperature increases and maximizing in refluxing toluene.[23] The bis(diazoketone)s having *trans*-cyclohexane and cyclohexene ring systems were the most reactive of those we examined. Thus, the general conditions for bis(diazoketone) reactions involved carrying out the reactions at 170 °C in a sealed tube. For example, a toluene solution of *cis*-1,2-bis(diazoketone) **14** heated at 170 °C resulted in a clean conversion to *cis*-hydroindenone **15**, whose ^1H NMR spectrum was identical to that of authentic material data.[24,25]

Properties of *trans*-Hydro-2-inden-1-ones. A number of methods have been developed for the efficient preparation of 4- and 5-substituted 2-cyclopentenones including 4,5-annelated compounds, with efforts being concentrated on controlling the regiochemistry of the double bond at the less substituted Δ^2−position.[26,27] As a result, *cis*-hydroindenone **15** has been efficiently synthesized by many reaction schemes.[24,27] However, *trans*-hydroindenone **1** has never been synthesized or even detected in the syntheses of **15**. Therefore, the facile production of *trans*-hydroindenones **1**, **2**, and **3** by the thermal reactions of **5**, **11**, and **12**, respectively, were remarkable. In order to gain insight into the structures and properties of **1** and **15**, we carried out their geometry optimization at the *ab initio* 3-21G(*) level and found that the energy preference of **15** over **1** was 5.0 kcal/mol.[21,28,29] These theoretical results were supported by the observation that treatment of **1** with DBU (1,8-diazabicyclo[5.4.0]-undecene) in benzene at room temperature caused complete isomerization to **15**. The weak acidic catalyst PPTS (pyridinium *p*-toluenesulfonate) also induced the partial isomerization (see the Experimental Section). With this experimental and theoretical data, it is conceivable that the absolutely neutral conditions, which suppress the enolization−isomerization pathway, were indispensable for the formation of *trans*-hydroindenones with complete stereospecificity during the thermal reactions of *trans*-1,2-bis(diazoketone)s.

Table 2. Syntheses of Acyclic Bis(diazoketone)s

diacid	bis(diazoketone)	yield (%)
		
16 : R = Ph **17** : R = n-$C_{10}H_{21}$	**18** : R = Ph **19** : R = n-$C_{10}H_{21}$	18[a] 12[b]
		
20	**21**	47[a]
		
22 : R = Ph **23** : R = n-$C_{10}H_{21}$	**24** : R = Ph **25** : R = n-$C_{10}H_{21}$	32[a] 40[a]

[a] CH_2N_2 [b] $LiC(N_2)SiMe_3$.

Thermal Reactions of Acyclic 1,2- and 1,3-Bis(diazoketone)s. Having examined the thermal reactions of cyclic 1,2-bis(diazoketone)s, we next investigated the reactions of acyclic 1,2-bis(diazoketone)s. These compounds were prepared from the corresponding diacid chlorides in modest yields (Table 2). The reactions of these acyclic 1,2-bis(diazoketone)s proceeded cleanly, with comparable yields to those of the cyclic cases (Table 3). These results indicated that despite our initial estimation, the flexible conformation of the acyclic 1,2-bis(diazoketone)s did not interfere with the cyclization process. Since reactions of symmetric bis(diazoketone)s afforded unsymmetric enones, two isomeric products were anticipated to form from the unsymmetric bis(diazoketone)s. The reaction of phenyl-substituted 1,2-bis(diazoketone) **18** afforded a mixture of 5-phenyl- and 4-phenylcyclopentenones **26** and **27** in a 48:52 ratio, respectively. A mixture of 5- and 4-decylcyclopentenones **28** and **29** was obtained from **19**, with **29** being the major product.

(21) Molecular orbital calculations were carried out using Spartan molecular modeling software (version 3.1). The optimized geometries were deposited in the supplementary material.

(22) Calculated dihedral angle of 3-H−C_3−C_{3a}−3a-H in the optimized structure of **3** at the 3-21G(*) level is 82.2°.

(23) Solvents (bp) and yields were as follows: benzene (80 °C), 36%; cyclohexane (81 °C), 25%; 1,2-dichloroethane (83 °C), 36%; *n*-heptane (98 °C), 43%; toluene (110 °C), 92%; isobutyl acetate (116 °C), 52%.

(24) (a) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642−2645. (b) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2377−2396. (b) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2397−2411. (d) Denmark, S. E.; Habermas, K. L.; Hite, G. A.; Jones, T. K. *Tetrahedron* **1986**, *42*, 2821−2829. (e) Denmark, S. E.; Habermas, K. L.; Hite, G. A. *Helv. Chim. Acta* **1988**, *71*, 168−194. (f) Denmark, S. E.; Hite, G. A. *Helv. Chim. Acta* **1988**, *71*, 195−208.

(25) Thermal reaction of **6** at 170 °C in toluene produces **1** with concomitant isomerization to **15**. Interestingly, thermal reaction of **14** in refluxing toluene gave **15** accompanied with **1** (~5%). These observations also confirmed the novel structure of **1**.

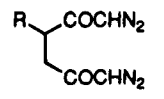
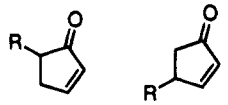
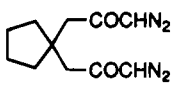
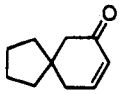
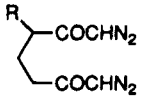
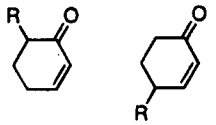
(26) Stork, G.; Nelson, G. L.; Rouessac, F.; Gringore, O. *J. Am. Chem. Soc.* **1971**, *93*, 3091−3092.

(27) (a) Noyori, R.; Ohnishi, Y.; Kato, M. *J. Am. Chem. Soc.* **1975**, *97*, 928−929. (b) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852−865. (c) Hiroi, K.; Sato, H.; Kotsuji, K. *Chem. Lett.* **1986**, 743−746. (d) Rizzo, C. J.; Dunlap, N. K.; Smith, A. B., III. *J. Org. Chem.* **1987**, *52*, 5280−5283.

(28) MM2 calculations done by Denmerk *et al.* showed that the energy preference of *cis*-C_{3a}-methyl substituted 2-inden-1-one over its *trans*-isomer was 2.76 kcal/mol (ca. 99:1 at 25 °C).[24e]

(29) In **15** the conformer bearing the carbonyl group at the pseudoaxial position was the most stable. The other chair conformer (the pseudoequatorial carbonyl group) was less stable by 1.8 kcal/mol.

Table 3. Thermal Reaction of Acyclic Bis(diazoketone)s[a]

bis(diazoketone)s	product(s)			yield (%)
				
18 : R = Ph	**26**	(48 : 52)[c]	**27**	82[b]
19 : R = n-$C_{10}H_{21}$	**28**	(32 : 68)[c]	**29**	81[b]
				
21	**30**			68
				
24 : R = Ph	**31**	(38 : 62)[d]	**32**	44[b]
25 : R = n-$C_{10}H_{21}$	**33**	(28 : 72)[d]	**34**	45[b]

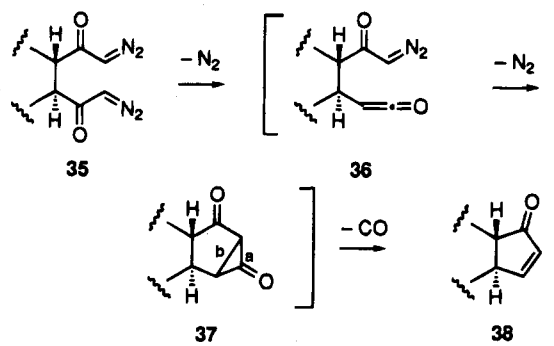
[a] Reactions were carried out by heating a toluene solution at 170 °C in a sealed tube. [b] Combined yield. [c] Determined by GLC. [d] Determined by ^{1}H NMR.

Table 4. Photochemical Cyclization of Bis(diazoketone)s[a]

bis(diazoketone)s	product(s)	yield (%)
5	**1**	23
12	**3**	54
18	**26** (42:58) **27**	40[b]
19	**28** (44:56) **29**	44[b]
24	**31** (40:60) **32**	18[b]
25	**33** (64:36) **34**	21[b]

[a] A toluene solution of bis(diazoketone) was irradiated with high pressure Hg lamp through Pyrex filter for 2 h. Product ratios were determined by ^{1}H NMR. [b] Combined yields.

Scheme 2



This developed methodology can also be used with 1,3-bis(diazoketone)s to produce cyclohexenone derivatives. 1,3-Bis(diazoketone)s were synthesized from the corresponding diacid chlorides in moderate yields (Table 2). Upon heating at 170 °C, symmetric 1;3-bis(diazoketone) **21** cleanly produced spiro cyclohexenone **30** as the sole product (Table 3). As expected, unsymmetric 1,3-bis(diazoketone)s produced a mixture of cyclohexenone regioisomers. In these cases, 4-substituted isomers (**32** and **34**) dominated over 6-substituted isomers. Since the initial step of the thermal reaction of a bis(diazoketone) is the Wolff rearrangement of one of the two diazoketone functionalities, the isomeric ratio of the reaction products of unsymmetric bis(diazoketone)s might be a function of the tendencies toward Wolff rearrangement of the two diazoketone functionalities (*e.g.*, α-substituted *vs* non-substituted). From this point of view, the α-substituted diazoketones would be more susceptible to the Wolff rearrangement, under these conditions.[30]

Photochemical Reactions of Bis(diazoketone)s. It is reported that the migratory aptitude of groups during the Wolff rearrangement may depend on the reaction conditions (*e.g.*, thermal *vs* photochemical).[2,31] To examine the photochemical behavior of 1,2- and 1,3-bis(diazoketone)s under photochemical conditions, they were irradiated in toluene with a high pressure mercury lamp through a Pyrex filter (Table 4). Under these photochemical conditions, the cyclizations proceeded to produce cyclopentenones and cyclohexenones with decreased efficiency. Although the ratios of the two isomeric products were different from those obtained under thermal conditions, unequivocal rationalizations of condition-dependent tendencies of migration during the Wolff rearrangement were not possible.

Aspects of the Thermal Cyclizations. The fact that symmetric bis(diazoketone)s gave unsymmetric enones indicated that these thermal reactions proceeded cooperatively between the ketene and the diazoketone functionality in the transient intermediate diazoketene **36** (Scheme 2). The subsequent decomposition of **36** might produce intermediate **37**, from which thermal elimination of carbon monoxide giving cyclopentenones is well precedented (Scheme 2).[32] While the mechanism of **36** → **37** is not clear, the remarkable efficiency of the formation of *trans*-hydroindenones suggested that the initial bond formation could be bond a, between the ketene *sp* carbon and the negatively charged diazo-bearing carbon, to form a six-membered carbocycle.[33] In spite of the diversity of possible intermolecular cooperative reactions,[7,8] the thermal reactions of 1,2-bis(diazoketones) proceeded quite efficiently. This fact suggests that the intramolecular directs the reaction to exclusive enone formation by eliminating other possible decomposition pathways.

While there are significant limitations to the preparations of *cis*-cyclic and acyclic 1,2-bis(diazoketone)s, the products of the thermal reactions of these bis(diazoketone)s can also be efficiently obtained by conventional synthetic methods. On the other hand, *trans*-1,2-bis(diazoketone)s are easily synthesized from the corresponding diacid chlorides and give unprecedented *trans*-hydroindenones. Therefore, the conventional methods and the thermal cyclizations we have developed are complementary. *Trans*-hydroindanones bearing an angular methyl group at the C_{7a} position are a well-known subunit in many naturally-occurring steroids and cyclopentanoids having significant biological activities. Accordingly, the thermal reactions of 1,2-bis(diazoketone)s

(30) Barker, W. D.; Gilbert R.; Lapointe, J. P.; Veschambre, H.; Vocelle, D. *Can. J. Chem.* **1969**, *47*, 2853–2858.
(31) Zeller, K.-P.; Meier, H.; Müller, E. *Tetrahedron* **1972**, *28*, 5831–5838.

(32) (a) Spencer, T. A.; Baldwin, S. W.; Schimegel, K. K. *J. Org. Chem.* **1965**, *30*, 1294–1296. (b) Spencer, T. A.; Hall, A. L.; Fordham, v Reyn, C. *J. Org. Chem.* **1968**, *33*, 3369–3373. (c) Büchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021–2023. (d) Kienzle, F.; Holland, G.; Jernow, J. L.; Kwoh, S.; Rosen, P. *J. Org. Chem.* **1973**, *38*, 3440–3442. (e) Büchi, G.; Hochstrasser, U.; Pawlak, W. *J. Org. Chem.* **1973**, *38*, 4348–4350.
(33) The bond a formation produced *trans*-bicyclo[4.4.0]decane system, of which formation would be easier than the direct formation of *trans*-bicyclo[4.3.0]nonane ring system by bond b connection.

now open the door for the synthesis of novel steroids and cyclopentanoid analogs without the angular methyl group, whose physiological and biological properties are of particular interest.[34]

Conclusion

We have examined the syntheses of 1,2-bis(diazoketone)s and their Wolff rearrangement under thermal and photochemical conditions. Thermal reactions provide facile access to various 2-cyclopenten-1-one derivatives in high yield with complete stereospecificity. Photochemical reactions also produce these enones but with lower efficiencies. The synthetic method that we report allows, for the first time, the synthesis of *trans*-hydroindenones without substituents at the ring junctures, whose acid and base sensitivities have prevented their synthesis by conventional methods. Accordingly, the thermal cyclization of *trans*-1,2-bis(diazoketone)s indispensably complements conventional methods for the synthesis of various 2-cyclopentenone derivatives and significantly expands the utility of α-diazoketones.

Experimental Section

Melting points were determined with a Yamato MP-21 melting point apparatus and are uncorrected. ^{1}H NMR spectra were measured with JEOL FX-100 (100 MHz) or JEOL JNM GX-400 (400 MHz) spectrometers. Coupling constants (*J* values) are reported in hertz. ^{13}C NMR spectra were measured with a JEOL JNM GX-400 (100 MHz) and JEOL FX-100 (25 MHz) spectrometers. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using tetramethylsilane (δ = 0) or residual chloroform (δ = 7.24) and benzene (δ = 7.15) as an internal standard. IR spectra were recorded on a JASCO A-102 spectrometer. Mass spectra were recorded on a JMS D-300 or AX-500. Gas liquid chromatography was carried out on Shimadu GC-8A using the column (2 m) equipped with OV-1. Fuji Davison Silica Gel BW-200 was used for silica gel flash chromatography. Precoated TLC plates Merck silica gel 60 F_{254} was used for preparative TLC. Anhydrous reactions were performed under N_2 atmosphere. Ether and tetrahydrofuran (THF) were distilled under N_2 from sodium/benzophenone ketyl prior to use. Calculations were performed on SGI INDY (R4000SC personal workstation) with Spartan molecular modeling software (*ver.* 3.1).

***trans*-1,1′-(1,2-Cyclohexanediyl)bis(2-diazoethanone) (5) (general procedure for diazoketone preparation using diazomethane).** To a suspension of ether (185 mL) and 40% aqueous potassium hydroxide (74 mL) was added *N*-methyl-*N*-nitrosourea (17.3 g, 0.17 mol) in portions at 0 °C with vigorous stirring. The ether layer was separated and dried over the pellets of sodium hydroxide. To the ethereal diazomethane solution was added a solution of *trans*-1,2-cyclohexanedicarbonyl chloride (**4**) (2.00 g, 4.6 mmol) in dry ether (100 mL) dropwise over 1 h under cooling with an ice–salt bath with vigorous stirring and the mixture was stirred overnight. Excess diazomethane and ether were removed by gentle heating to concentrate to the one-third of the volume. The residual solution was filtered and concentrated *in vacuo*. Flash chromatograpy (SiO_2, hexane:EtOAc = 2:1) of the residue gave **5** (1.02 g, 48%) as yellow solids. Analytical sample of **5** was obtained by recrystallization from ether giving yellow prisms: mp 80 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.10–1.21 (4H), 1.75–1.90 (4H), 2.61 (br, 2H), 5.27 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 25.3, 29.5, 49.8, 54.8, 197.2; IR ($CHCl_3$) 2930, 2850, 2105, 1635, 1445, 1365, 1340, 1142, 910 cm^{-1}; MS *m/z* (%) 192 [(M − N_2)$^+$] (15), 164 [(M − N_4)$^+$] (15), 149 (16), 135 (37), 107 (38), 91 (32), 79 (100), 67 (77), 59 (71). Anal. Calcd for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.52; H, 5.49; N, 25.37.

***trans*-3a,4,5,6,7,7a-Hexahydro-1*H*-inden-1-one (1) (general procedure for thermal reaction in refluxing toluene).** A solution of **5** (30.0 mg, 0.14 mmol) in toluene (14 mL, 0.01 M) was heated at reflux for 6 h under Ar atmosphere. After concentration *in vacuo*, flash chromatograpy (SiO_2, hexane:EtOAc = 20:1) of the residue gave **1** (17.0 mg, 92%) as a colorless oil, which solidified in a refrigerator: ^{1}H NMR ($CDCl_3$) δ 1.32–1.40 (4H), 1.90–1.96 (3H), 2.07–2.13 (2H), 2.36 (m, 1H), 6.03 (dd, 1H, *J* = 6.1, 2.4 Hz), 7.46 (d, 1H, *J* = 6.1 Hz); ^{13}C NMR ($CDCl_3$) δ 23.8, 26.2, 26.7, 30.1, 48.1, 56.6, 132.8, 161.8, 208.1; IR ($CDCl_3$) 2930, 2850, 1700, 1560, 1440, 1355, 1175, 860, 805 cm^{-1}; MS *m/z* (%) 136 (M$^+$) (100), 107 (97), 95 (50), 79 (48), 68 (18), 55 (23); HRMS calcd for $C_9H_{12}O$ (M$^+$) 136.0888, found 136.0904.

***trans*-1,2-Cyclohex-4-enedicarbonyl Chloride (9).** To a solution of 1,3-butadiene (**6**) (1.83 g, 33.9 mmol) in benzene (20 mL) was added fumaryl chloride (**8**) (4.31 g, 28.2 mmol, 3.1 mL) at −78 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was concentrated *in vacuo*. Distillation of the residue (114–115 °C/7 mmHg) gave **9** (5.41 g, 93%) as colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.24–2.42 (2H), 2.64–2.80 (2H), 3.32–3.42 (2H), 5.72–5.82 (2H); ^{13}C NMR ($CDCl_3$) δ 27.4, 52.7, 124.1, 175.3; IR (neat) 3050, 2935, 1780, 1660, 1440, 1285, 1025 cm^{-1}; MS *m/z* (%) 171 [(M − ^{35}Cl)$^+$] (24), 142 (22), 114 (24), 107 (9), 79 (100). Anal. Calcd for $C_8H_8Cl_2O_2$: C, 46.41; H, 3.89. Found: C, 46.31; H, 3.88.

***trans*-1,1′-(4-Cyclohexene-1,2-diyl)bis(2-diazoethanone) (11).** To the ethereal diazomethane solution prepared from *N*-methyl-*N*-nitrosourea (10.5 g, 0.10 mol) was added a solution of **9** (1.20 g, 5.80 mmol) in dry ether (20 mL) dropwise over 1 h under cooling with an ice–salt bath with vigorous stirring, and the mixture was stirred overnight. Excess diazomethane and ether were removed by gentle heating at about 40 °C. After filtration and concentration flash chromatography (SiO_2, hexane:EtOAc = 3:1) of the residue gave **11** (433 mg, 34%) as yellow prisms. Analytical sample was obtained by recrystallization from ether: mp 75 °C dec; ^{1}H NMR (C_6D_6) δ 1.90 (m, 2H), 2.09 (m, 2H), 2.63 (br, 2H), 4.47 (m, 2H), 5.49 (m, 2H); ^{13}C NMR (C_6D_6) δ 28.8, 46.7, 54.0, 125.3, 195.8; IR (C_6H_6) 3015, 2910, 2205, 1643, 1365, 1335, 1142 cm^{-1}; MS *m/z* (%) 190 [(M − N_2)$^+$] (25), 162 (9), 133 (70), 105 (82), 91 (63), 79 (100), 69 (38), 65 (23), 55 (33). Anal. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.91; H, 4.57; N, 25.66.

***trans*-3a,4,7,7a-Tetrahydro-1*H*-inden-1-one (2).** Since the product **2** was volatile, reaction of **11** (58.5 mg, 0.27 mmol) was carried out in benzene (27 mL) following the procedure of **14** to give **2** (30.5 mg, 85%) after flash chromatography (SiO_2, pentane:ether = 20:1): ^{1}H NMR ($CDCl_3$) δ 2.10–2.29 (3H), 2.38–2.50 (2H), 2.67 (m, 1H), 5.78 (m, 1H), 5.83 (m, 1H), 6.14 (dd, 1H, *J* = 6.1, 2.4 Hz), 7.56 (d, 1H, *J* = 5.5 Hz); ^{13}C NMR ($CDCl_3$) δ 24.6, 30.1, 43.8, 51.6, 127.4, 128.2, 133.6, 161.2, 208.0; IR ($CDCl_3$) 3030, 2930, 2850, 1710, 1440, 1360, 835 cm^{-1}; MS *m/z* (%) 134 (M$^+$) (100), 119 (18), 105 (32), 91 (53), 79 (34), 65 (9), 55 (12), 51 (15); HRMS calcd for $C_9H_{10}O$ (M$^+$) 134.0732, found 134.0750.

***trans*-4,5-Dimethyl-1,2-cyclohex-4-enedicarbonyl Chloride (10).** A solution of **7** (728 mg, 1.0 mL, 8.6 mmol) and fumaryl chloride (**8**) (1.09 g, 7.1 mmol) in benzene (20 mL) was stirred 2 days at room temperature. The reaction mixture was concentrated *in vacuo*. Distillation of the residue (137–138 °C/7 mmHg) gave **10** (1.27 g, 76%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3H × 2), 2.16–2.33 (2H), 2.44–2.57 (2H), 3.26–3.36 (2H); ^{13}C NMR ($CDCl_3$) δ 18.6, 33.3, 53.6, 123.6, 175.3; IR (C_6D_6) 2925, 2850, 1785, 1440, 1025, 1005, 850, 780 cm^{-1}; MS *m/z* (%) 234 (M$^+$) (15), 199 (7), 170 (11), 143 (19), 135 (10), 107 (100), 91 (30); HRMS calcd for $C_{10}H_{12}O_2{}^{35}Cl_2$ (M$^+$) 234.0214, found 234.0226. Anal. Calcd for $C_{10}H_{12}O_2Cl_2$: C, 51.09; H, 5.14. Found: C, 51.35; H, 5.21.

***trans*-1,1′-(4,5-Dimethyl-4-cyclohexene-1,2-diyl)bis(2-diazoethanone) (12).** By following the procedure for the reaction of **4**, **12** (131 mg, 21%) was obtained as yellow prisms by the reaction of **10** (600 mg, 2.55 mmol) with the ethereal diazomethane solution prepared from *N*-methyl-*N*-nitrosourea

(34) For synthesis of compounds structurally related to steroids, see Woski, S. A.; Koreeda, M. *J. Org. Chem.* **1992**, *57*, 5736–5741 and references therein.

(4.62 g, 45.7 mmol) followed by flash chromatography (SiO_2, hexane:EtOAc = 3:1): mp 92 °C dec; ^1H NMR ($CDCl_3$) δ 1.44 (s, 3H × 2), 1.71–1.86 (2H), 1.95–2.14 (2H), 2.66 (br, 2H), 4.75–4.80 (2H); ^{13}C NMR (C_6D_6) δ 18.6, 35.1, 47.5, 54.0, 124.1, 196.1; IR (C_6D_6) 3125, 2930, 2120, 1640, 1370, 1340, 1140 cm^{-1}; MS *m/z* (%) 190 [$(M - N_4)^+$] (15), 175 (26), 162 (12), 147 (43), 133 (38), 117 (37), 105 (61), 91 (100), 79 (44), 68 (47), 55 (58).

***trans*-5,6-Dimethyl-3a,4,7,7a-tetrahydro-1*H*-inden-1-one (3).** By following the procedure for the reaction of **5**, **3** (11.2 mg, 53%) was obtained from **12** (32.2 mg, 0.13 mmol) as colorless prisms. An X-ray sample was recrystallized from ether: mp 70.0–71.0 °C; ^1H NMR ($CDCl_3$) δ 1.66 (s, 3H × 2), 2.04–2.30 (5H), 2.53–2.62 (m, 1H), 6.08 (dd, 1H, J = 5.8, 2.7 Hz), 7.51 (d, 1H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.5 × 2, 30.4, 36.2, 44.5, 52.3, 126.5, 127.3, 133.7, 161.2, 208.3; IR ($CHCl_3$) 3000, 2910, 2840, 1705, 1440, 1205, 838 cm^{-1}; MS *m/z* (%) 162 (M^+) (100), 147 (81), 129 (10), 119 (33), 105 (18), 91 (33), 82 (10), 79 (20), 77 (19), 67 (28), 57 (25), 55 (55); HRMS calcd for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1027.

***cis*-Cyclohexanedicarbonyl Chloride (13) (general procedure for acid chloride preparation with PCl_5).** The mixture of *cis*-cyclohexanedicarboxylic acid (5.00 g, 29.0 mmol) and phosphorus pentachloride (12.1 g, 58.0 mmol) was stirred overnight at room temperature. After removing phosphorus oxychloride *in vacuo*, the residue was diluted with hexane, washed with cold water and brine, dried over anhydrous $MgSO_4$, and filtered. **13** (5.60 g, 93%) was obtained as colorless oil by concentration of the filtrate and used in the next reaction without further purification: ^1H NMR ($CDCl_3$) δ 1.60–1.82 (m, 4H), 1.75–2.00 (m, 2H), 2.27–2.57 (m, 2H), 3.40–3.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.6, 40.4, 172.9; IR (neat) 2930, 2850, 1780, 1450, 1220, 980, 905 cm^{-1}; MS *m/z* (%) 173 [$(M - {}^{35}Cl)^+$] (23), 144 [$(M - CO^{35}Cl)^+$] (18), 116 (17), 109 (22), 81 (100), 67 (17); HRMS calcd for $C_8H_{10}{}^{37}ClO_2$ [$(M - {}^{37}Cl)^+$] 175.0340, found 175.0322, calcd for $C_8H_{10}{}^{35}ClO_2$ [$(M - {}^{35}Cl)^+$] 173.0369, found 173.0365.

***cis*-1,1′-(1,2-Cyclohexanediyl)bis(2-diazoethanone) (14).** To a solution of diisopropylamine (0.40 mL, 2.87 mmol) in dry ether (6 mL) was added *n*-butyllithium (1.6 M in hexane, 1.80 mL, 2.87 mmol) dropwise, and the mixture was stirred for 15 min at −78 °C. The resulting solution was added dropwise to a solution of (phenyldimethylsilyl)diazomethane (506 mg, 2.87 mmol) in dry ether (6 mL) at −78 °C, and the mixture was stirred for 1 h at 0 °C. The resulting solution of lithiated (phenyldimethylsilyl)diazomethane was added dropwise to a solution of **13** (300 mg, 1.43 mmol) in dry ether (6 mL) at −78 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with ether, washed with water and brine, and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated *in vacuo*. Flash chromatography (SiO_2, hexane:EtOAc = 3:1) of the residue gave **14** (86.0 mg, 27%) as yellow solids, which was recrystallized from ether giving yellow prisms: mp 80.8–81.5 °C; ^1H NMR ($CDCl_3$) δ 1.31–1.38 (2H), 1.52–1.66 (4H), 1.90–2.05 (2H), 2.71 (br, 2H), 5.33 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 23.3, 26.7, 47.7, 53.9, 196.7; IR ($CHCl_3$) 2950, 2150, 1635, 1450, 1365, 1325, 1150 cm^{-1}; MS *m/z* (%) 192 [$(M - N_2)^+$] (8), 164 [$(M - N_4)^+$] (8), 149 (17), 135 (28), 123 (10),107 (31), 91 (36), 79 (100), 67 (80), 58 (58). Anal. Calcd for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.43; H, 5.52; N, 25.14.

***cis*-3a,4,5,6,7,7a-Hexahydro-1*H*-inden-1-one (15) (general procedure for thermal reaction at 170 °C).** A solution of **14** (31.0 mg, 0.14 mmol) in toluene (14 mL, 0.01 M) was heated at 170 °C for 20 min in a sealed tube. After it was cooled, the reaction mixture was concentrated *in vacuo*. Flash chromatography (SiO_2, hexane:EtOAc = 20:1) of the residue gave **15** (13.6 mg, 71%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.07–1.56 (5H), 1.69 (m, 1H), 1.82–1.99 (3H), 2.38 (q, 1H, J = 6.3 Hz), 2.95 (m, 1H), 6.13 (dd, 1H, J = 5.5, 1.8 Hz), 7.62 (dd, 1H, J = 5.5, 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.4, 22.6, 28.2, 41.0, 45.4, 132.3, 167.7, 212.0; IR ($CDCl_3$) 2930, 2850, 1700, 1585, 1450, 1355, 1190, 1170, 805 cm^{-1}; MS *m/z* (%) 136 (M^+) (100), 107 (97), 95 (50), 79 (56), 67 (20), 55 (20); HRMS calcd for $C_9H_{12}O$ (M^+) 136.0888, found 136.0884.

Isomerization of 1. (a) DBU treatment: To a solution of **1** (23.5 mg, 0.17 mmol) in benzene (2 mL) was added DBU (3.3 mg, 0.02 mmol, 3 μL), and the mixture was stirred for 96 h at room temperature. The reaction was quenched with small amount of dilute HCl and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and filtered. Concentration of filtrate *in vacuo* gave a crude product (21.3 mg, 91%), which was exclusively *cis*-isomer **15** by ^1H NMR.

(b) PPTS treatment: To a solution of **1** (13.9 mg, 0.10 mmol) in benzene (2 mL) was added PPTS (5.0 mg, 0.02 mmol), and the mixture was stirred for 48 h at room temperature. The reaction was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and filtered. Concentration of filtrate *in vacuo* gave a crude product (11.5 mg, 83%), which was a mixture of **1** and **15** (ca. 1:1) by ^1H NMR.

1,6-Didiazo-3-phenyl-2,5-hexanedione (18). By following the procedure for the reaction of **4**, **18** (401 mg, 18%) as a pale yellow oil was obtained by the reaction of phenylsuccinyl chloride (2.21 g, 9.6 mmol) and ethereal diazomethane prepared from *N*-methyl-*N*-nitrosourea (17.3 g, 0.17 mol) followed by flash chromatography (SiO_2, benzene:EtOAc = 2:1): ^1H NMR (C_6D_6) δ 2.18 (dd, 1H, J = 16.5, 4.9 Hz), 3.00–3.22 (m, 1H), 3.96–4.14 (br, 1H), 4.26 (s, 1H), 4.29 (s, 1H), 6.92–7.12 (5H); ^{13}C NMR (C_6D_6) δ 43.5, 52.0, 54.0, 54.6, 127.7, 128.4, 129.2, 139.1, 191.8, 193.1; IR (C_6H_6) 2105, 1643, 1358, 1140, 1072, 810 cm^{-1}; MS *m/z* (%) 242 (M^+) (0.8), 214 [$(M - N_2)^+$] (8), 186 (11), 157 (24), 144 (17), 129 (57), 115 (75), 103 (37), 91 (22), 82 (26), 77 (38), 69 (100); HRMS calcd for $C_{12}H_{10}N_2O_2$ [$(M - N_2)^+$] 2214.0743, found 214.0734.

5-Phenyl-2-cyclopenten-1-one (26) and 4-Phenyl-2-cyclopenten-1-one (27). By following the procedure for the reaction of **14**, a mixture of **26** and **27** (32.7 mg, 82% combined yield, 48:52 by ^1H NMR) was obtained by starting from **18** (61.4 mg, 0.25 mmol). **26**: ^1H NMR ($CDCl_3$) δ 2.82 (dq, 1H, J = 19.5, 2.4 Hz), 3.25 (ddt, 1H, J = 19.5, 7.3, 2.4 Hz), 3.54 (dd, 1H, J = 7.3, 2.4 Hz), 6.29 (dt, 1H, J = 5.5, 2.3 Hz), 7.15 (d, 1H, J = 7.3 Hz), 7.24 (t, 1H, J = 7.0 Hz), 7.32 (t, 1H, J = 7.6 Hz), 7.84 (dt, 1H, J = 5.7, 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ 38.7, 50.9, 127.0, 127.6, 128.9, 129.0, 133.7, 163.6 (carbonyl carbon could not be observed); IR ($CHCl_3$) 2930, 2850, 1705, 1665, 1590, 1503, 1355, 1170 cm^{-1}; MS *m/z* (%) 158 (M^+) (100), 129 (92), 115 (42), 103 (15), 78 (18). **27**: ^1H NMR ($CDCl_3$) δ 2.33 (dd, 1H, J = 18.7, 2.8 Hz), 2.90 (dd, 1H, J = 18.9, 6.7 Hz), 4.17 (dq, 1H, J = 6.7, 2.4 Hz), 6.32 (dd, 1H, J = 5.8, 2.1 Hz), 7.15 (d, 2H, J = 6.7 Hz), 7.24–7.29 (1H, signal obscured by $CHCl_3$), 7.34 (t, 2H, J = 7.6 Hz), 7.67 (dd, 1H, J = 5.5, 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 44.0, 46.8, 77.3, 127.1, 127.3, 129.0, 134.1, 166.4 (carbonyl carbon could not be observed); IR ($CDCl_3$) 2930, 1708, 1585, 1493, 1400, 1350, 1180 cm^{-1}; MS *m/z* (%) 158 (M^+) (68), 130 [$(M - CO)^+$] (100), 115 (56), 103 (23), 77 (21).[35]

1,6-Didiazo-3-decyl-2,5-hexanedione (19). A mixture of commercially available decylsuccinic anhydride (5.00 g, 20.8 mmol) and water (30 mL) was heated at reflux overnight. After being cooled, the resulting precipitate was collected by filtration and washed with cold water (×3). Drying the filtered solid under reduced pressure gave crystalline decylsuccinic acid (5.58 g, 100%). By following the procedure for the preparation of **13**, decylsuccinic acid (300 mg, 1.17 mmol) was transformed with phosphorus pentachloride (536 mg, 2.57 mmol) into the corresponding diacid chloride **17** (345 mg, 100%). To a solution of diisopropylamine (0.50 mL, 4.1 mmol) in dry ether (10 mL), *n*-butyllithium (1.6 M in hexane , 2.6 mL, 4.1 mmol) was added dropwise, and the solution was stirred for 15 min at −78 °C. The resulting solution was added dropwise to a solution of (trimethylsilyl)diazomethane (465 mg, 4.1 mmol) in dry ether (10 mL) at −78 °C, and the mixture was stirred for 1 h at 0 °C. The resulting solution of lithiated (trimethylsilyl)diazomethane was added dropwise to a solution of **17** (600 mg, 2.0

(35) While we have tried combustion and/or HRMS analysis, satisfactory data could not be obtained.

(36) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

mmol) in dry ether (10 mL) at −78 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with ether, washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography (SiO_2, hexane:EtOAc = 3:1) of the residue gave **19** (76.0 mg, 12%) as a yellow oil: ^1H NMR (C_6D_6) δ 0.91 (t, 3H, J = 6.7 Hz), 1.06−1.64 (18H), 1.95 (dd, 1H, J = 15.9, 4.3 Hz), 2.54 (br, 1H), 2.80 (br, 1H), 4.28 (s, 1H), 4.51 (s, 1H); ^{13}C NMR (C_6D_6) δ 14.3, 23.1, 27.4, 29.7, 29.8, 30.0, 30.1 (×2), 32.3, 32.8, 42.5, 45.7, 53.9, 54.0, 191.9, 196.1; IR (C_6H_6) 2945, 2870, 2100, 1738, 1640, 1358, 1320 cm^{-1}; MS *m/z* (%) 291 [(M − Me)$^+$] (7), 279 (26), 251 (100), 223 (47).

5-Decyl-2-cyclopenten-1-one (28) and 4-Decyl-2-cyclopenten-1-one (29). By following the procedure for the reaction of **14**, an inseparable mixture of **28** and **29** (20.4 mg, 79% combined yield, 32:68 by ^1H NMR) was obtained from **19** (35.6 mg, 0.12 mmol). **28**: ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 6.1 Hz), 1.10−1.18 (18H), 2.27 (m, 1H), 2.33 (dq, 1H, J = 19.2, 2.1 Hz), 2.83 (ddt, 1H, J = 19.2, 6.4, 2.4 Hz), 6.14 (dt, 1H, J = 5.5, 2.1 Hz), 7.64 (dt, 1H, J = 5.5, 2.4 Hz); GC-MS *m/z* (%) 222 (M$^+$) (22), 109 (22), 95 (87), 82 (100), 67 (13), 55 (15); HRMS calcd for $C_{15}H_{26}O$ (M$^+$) 222.1985; found 222.1954. **29**: ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 6.1 Hz), 1.10−1.18 (18H), 1.97 (dd, 1H, J = 18.6, 2.1 Hz), 2.50 (dd, 1H, J = 19.0, 6.0 Hz), 2.89 (m, 1H), 6.11 (dd, 1H, J = 5.5, 1.8 Hz), 7.61 (dd, 1H, J = 6.1, 2.4 Hz); GC-MS *m/z* (%) 222 (M$^+$) (2), 95 (23), 82 (100); HRMS calcd for $C_{15}H_{26}O$ (M$^+$) 222.1985, found 222.1955. As a mixture of **28** and **29**: ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 27.3, 27.6, 29.3, 29.5, 29.6, 29.8, 29.9, 31.3, 31.9, 32.0, 34.8, 35.8, 41.0, 41.1, 41.5, 45.0, 76.7, 76.8, 133.5, 133.9, 163.3, 168.6, 210.0, 212.6; IR ($CHCl_3$) 2930, 2845, 1703, 1585, 1460, 1345, 1170, 1060, 905, 810 cm^{-1}.

1,1′-Cyclopentylidenebis(3-diazo-2-propanone) (21). By following the procedure for the preparation of **13**, cycloheptanediacetic acid (2.00 g, 10.7 mmol) was transformed with phosphorus pentachloride (4.47 g, 21.5 mmol) into the corresponding diacid chloride **20** (2.16 g, 91%). By following the procedure for the reaction of **4**, **21** (196 mg, 47%) was obtained as a yellow oil by the reaction of **20** (400 mg, 1.79 mmol) and the etheral diazomethane solution prepared from *N*-methyl-*N*-nitrosourea (3.25 g, 32.1 mmol) followed by flash chromatography (SiO_2, hexane:EtOAc = 3:1): ^1H NMR (C_6D_6) δ 1.49 (br, 8H), 2.29 (br, 4H), 4.72 (br, 2H); ^{13}C NMR (C_6D_6) δ 23.9, 38.5, 45.1, 47.6, 54.7, 193.8; IR (C_6H_6) 2940, 2850, 2100, 1630, 1353, 1305, 1130 cm^{-1}; MS *m/z* (%) 178 [(M − N_4)$^+$] (12), 149 (18), 121 (20), 107 (30), 81 (48), 79 (58), 67 (100); HRMS calcd for $C_{11}H_{14}O_2$ [(M − N_4)$^+$] 178.0994, found 178.0983.

Spiro[4.5]-8-decen-7-one (30). By following the procedure for the reaction of **14**, **30** (16.5 mg, 68%) was obtained from **21** (37.5 mg, 0.16 mmol): ^1H NMR ($CDCl_3$) δ 1.41−1.53 (4H), 1.58−1.69 (4H), 2.31 (dd, 2H, J = 4.4, 1.8 Hz), 2.36 (s, 2H), 6.00 (dt, 1H, J = 10.2, 2.0 Hz), 6.88 (dt, 1H, J = 10.0, 4.1 Hz); ^{13}C NMR ($CDCl_3$) δ 24.1, 38.3, 38.6, 44.8, 56.2, 129.7, 149.2, 200.1; IR ($CDCl_3$) 2940, 2850, 1670, 1383, 1245, 1163, 885 cm^{-1}; MS *m/z* (%) 150 (M$^+$) (22), 108 (10), 79 (12), 68 (100); HRMS calcd for $C_{10}H_{14}O$ (M$^+$) 150.1045, found 150.1041.

1,7-Didiazo-3-phenyl-2,6-heptanedione (24). To a solution of 2-phenylglutaric acid (1.00 g, 4.80 mmol) in chloroform (10 mL) was added phosphorus pentachloride (2.00 g, 9.61 mmol) slowly at room temperature and stirred overnight. Chloroform and phosphorus oxychloride was evaporated *in vacuo*, the residue was diluted with hexane and washed by cold water (×3) and then brine, and dried over anhydrous $MgSO_4$. After filtration, concentration of the filtrate afforded 2-phenylglutaryl chloride **22** (812 mg, 69%). By following the procedure for the reaction of **4**, **24** (201 mg, 32%) was obtained as a yellow oil by the reaction of **22** (600 mg, 2.45 mmol) with the ethereal diazomethane solution prepared from *N*-methyl-*N*-nitrosourea (4.43 g, 43.8 mmol) followed by flash chromatography (SiO_2, hexane:EtOAc = 2:1): ^1H NMR (C_6D_6) δ 1.91 (t, 2H, J = 6.4 Hz), 2.00 (dt, J = 14.0, 7.3 Hz), 2.38 (dt, 1H, J = 13.9, 6.9 Hz), 3.36 (br, 1H), 4.15 (s, 1H), 4.27 (s, 1H), 7.02−7.18 (5H); ^{13}C NMR (C_6D_6) δ 27.8, 37.7, 53.4, 54.2, 55.5, 124.5, 128.4, 129.0, 139.2, 193.2, 193.6; IR (C_6H_6) 3005, 2905, 2080, 1645, 1355, 1140 cm^{-1}; MS *m/z* (%) 214 [(M − CH_2N_2)$^+$] (8), 186 (9), 158 (68), 129 (97), 115 (100), 103 (52), 91 (26), 77 (56), 69 (97), 63 (23), 55 (30), 51 (54); HRMS calcd for $C_{12}H_{10}N_2O_2$ [(M − CH_2N_2)$^+$] 214.0742, found 214.0751.

6-Phenyl-2-cyclohexan-1-one (31) and 4-Phenyl-2-cyclohexan-1-one (32). By following the procedure for the reaction of **14**, a mixture of **31** and **32** (13.8 mg, 44% combined yield, 38:62 by ^1H NMR) was obtained from **24** (46.2 mg, 0.18 mmol). They could be separated by preparative TLC (hexane:EtOAc = 5:1 with developing three times). **31**: ^1H NMR ($CDCl_3$) δ 2.26−2.33 (2H), 2.44−2.52 (2H), 3.61 (t, 1H, J = 7.9 Hz), 6.17 (dt, 1H, J = 10.2, 2.0 Hz), 7.04 (dt, 1H, J = 10.0, 4.1 Hz), 7.16 (d, 2H, J = 7.3 Hz), 7.23−7.28 (m, 1H, signal obscured by $CHCl_3$), 7.33 (t, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 25.5, 30.7, 53.4, 127.0, 128.3, 128.5, 130.3, 139.4, 149.9, 199.3; IR ($CHCl_3$) 3000, 2930, 1668, 1600, 1495, 1228 cm^{-1}; MS *m/z* (%) 172 (M$^+$) (68), 104 (83), 68 (100); HRMS calcd for $C_{12}H_{12}O$ (M$^+$) 172.0888, found 172.0891. **32**: ^1H NMR ($CDCl_3$) δ 2.16 (dddd, 1H, J = 13.0, 11.6, 9.5, 4.9 Hz), 2.37 (m, 1H), 2.43−2.60 (2H), 3.73 (m, 1H), 6.17 (dd, 1H, J = 9.8, 2.4 Hz), 6.99 (m, 1H), 7.22 (d, 2H, J = 7.3 Hz), 7.29 (d, 1H, J = 7.3 Hz), 7.36 (t, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 32.5, 37.0, 42.7, 127.1, 127.6, 128.9, 130.0, 142.8, 152.8, 199.2; IR ($CHCl_3$) 3020, 2940, 1675, 1450, 1390, 1200, 720 cm^{-1}; MS *m/z* (%) 172 (M$^+$) (65), 144 (20), 130 (100), 115 (21); HRMS calcd for $C_{12}H_{12}O$ (M$^+$) 172.0888, found 172.0880.

1,7-Didiazo-3-decyl-2,6-heptanedione (25). To a solution of sodium (329 mg, 14.3 mmol) in dry methanol (30 mL) was added a solution of dimethyl decylmalonate (4.58 g, 16.8 mmol) and methyl acrylate (1.20 g, 1.26 mL, 37.4 mmol) in MeOH (5 mL), and the mixture was heated at reflux overnight. The reaction mixture was neutralized with 2 N HCl and concentrated *in vacuo*. The residue was extracted with hexane−EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated *in vacuo*. Distillation of the residue under reduced pressure (bp 192−193 °C/1 mmHg) gave dimethyl 2-decyl-2-carbomethoxyglutarate (3.21 g, 64%): ^1H NMR ($CDCl_3$) δ 0.83 (t, 3H, J = 6.7 Hz), 1.06−1.30 (16H), 1.76−1.86 (2H), 2.12−2.28 (4H), 3.67 (s, 3H), 3.69 (s, 3H × 2); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 24.0, 27.8, 29.3, 29.4, 29.5, 29.5, 29.7, 31.8, 33.2, 51.6, 52.3, 56.9, 171.7, 173.1; IR (neat) 2950, 2925, 1738, 1453, 1435, 1380, 1198, 1170, 1125, 1090, 1020, 992, 890, 855, 850, 830, 820, 795 cm^{-1}. A suspension of dimethyl 2-decyl-2-carbomethoxyglutarate (827 mg, 2.31 mmol) in concentrated hydrochloric acid and acetic acid (1:1, 30 mL) was heated at reflux for 48 h, and the resulting mixture was concentrated *in vacuo*. Flash chromatography (SiO_2, hexane: EtOAc = 1:1) of the residue gave 2-decylglutaric acid (616 mg, 98%). For identification, this compound was transformed into dimethyl ester with diazomethane. Dimethyl 2-decylglutarate: ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 6.7 Hz), 1.14−1.66 (18H), 1.74−1.93 (m, 2H), 2.19−2.41 (3H), 3.64 (s, 3H), 3.65 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 26.7, 27.2, 29.3, 29.4, 29.5, 30.0, 31.8, 31.9, 32.3, 44.8, 51.5, 51.6, 173.5, 176.1; IR ($CDCl_3$) 2940, 2875, 1735, 1440, 1370, 1260, 1205, 1165, 1080, 890, 700 cm^{-1}. By following the procedure for the preparation of **13**, 2-decylglutaryl chloride (**23**) (495 mg, 87%) was obtained from 2-decylglutaric acid (500 mg, 1.84 mmol) and phosphorus pentachloride (765 mg, 3.67 mmol). By following the procedure for the reaction of **4**, **25** was obtained as yellow solids by the reaction of **23** (411 mg, 1.33 mmol) and the ethereal diazomethane solution prepared from *N*-methyl-*N*-nitrosourea (2.41 g, 23.8 mmol) followed by flash chromatography (SiO_2, hexane:EtOAc = 2:1). Recrystallization of **25** from ether afforded pale yellow plates: mp 50.5−52.0 °C; ^1H NMR (C_6D_6) δ 0.91 (t, 3H, J = 6.7 Hz), 1.13−1.34 (17H), 1.55 (m, 1H), 1.69 (ddt, 1H, J = 13.8, 7.6, 4.9 Hz), 1.82 (m, 1H), 1.89−2.05 (m, 2H), 2.13 (br, 1H), 4.24 (s, 1H), 4.42 (s, 1H); ^{13}C NMR (C_6D_6) δ 14.3, 23.0, 27.5, 27.6, 29.7, 29.8, 30.0 (×2), 30.1, 32.3, 32.9, 38.0, 38.1, 50.1, 53.3, 192.9, 196.7; IR (C_6H_6) 2900, 2850, 2090, 1640, 1323, 1138, 1103 cm^{-1}. Anal. Calcd for $C_{17}H_{28}N_4O_2$: C, 63.72; H, 8.81; N, 17.48. Found: C, 63.38; H, 8.81; N, 17.46.

6-Decyl-2-cyclohexen-1-one (33) and 4-Decyl-2-cyclohexen-1-one (34). By following the procedure for the reaction of **14**, a mixture of **33** and **34** (6.6 mg, 45% combined yield, 28:72 by ^1H NMR) was obtained from **25** (19.6 mg, 0.06 mmol). They could be separated by preparative TLC (hexane:EtOAc

= 5:1 with developing three times). **33**: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, J = 7.0 Hz), 1.17–1.43 (17H), 1.73 (dddd, 1H, J = 13.7, 10.4, 8.5, 5.5 Hz), 1.79 (m, 1H), 2.08 (dq, 1H, 13.4, 4.5 Hz), 2.18–2.40 (3H), 5.95 (dt, 1H, J = 10.2, 2.1 Hz), 6.88 (dt, 1H, J = 9.8, 4.7 Hz); ^{13}C NMR (C_6D_6) δ 14.1, 22.7, 25.0, 27.0, 27.7, 29.2, 29.3, 29.6 × 2, 29.7, 31.9, 46.6, 129.6, 149.2, 202.0 (One carbon signal could not be read.); IR ($CDCl_3$) 2940, 2870, 1672, 1460, 1392, 1225, 888 cm^{-1}; MS *m/z* (%) 236 (M^+) (12), 152 (7), 101 (73), 96 (100), 68 (42); HRMS calcd for $C_{16}H_{28}O$ 236.2141, found 236.2147. **34**: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 3.0 Hz), 1.14–1.54 (18H), 2.07 (dddd, 1H, J = 13.4, 9.8, 4.9, 1.2 Hz), 2.32 (ddd, 1H, J = 16.7, 12.1, 4.9 Hz), 2.35 (m, 1H), 2.46 (dt, 1H, 16.9, 4.9 Hz), 5.94 (dd, 1H, J = 10.1, 2.1 Hz), 6.82 (ddd, 1H, J = 10.2, 2.6, 1.4 Hz); ^{13}C NMR (C_6D_6) δ 14.1, 22.7, 27.0, 28.6, 29.3, 29.5, 29.6 × 2, 31.9, 34.6, 36.1, 37.0, 128.9, 155.2, 199.9 (One carbon signal could not be read.); IR ($CDCl_3$) 2930, 2860, 1675, 1458, 1420, 1395, 1352, 1260, 1215, 1148, 1130, 890, 795, 700 cm^{-1}; MS *m/z* (%) 236 (M^+) (32), 178 (8), 109 (82), 96 (100), 82 (26), 68 (55); HRMS calcd for $C_{16}H_{28}O$ 236.2141, found 236.2129.

Photochemical Cyclization of 1,2- and 1,3-Didiazo Diketones (general procedure). A solution of bis(diazoketone) dissolved in toluene (0.01 M) in a Pyrex vessel was irradiated with a high pressure Hg lamp for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed on silica gel giving **1** (4.7 mg, 23%) from **5** (33.3 mg, 0.15 mmol), **3** (9.9 mg, 54%) from **12** (27.8 mg, 0.11 mmol), a mixture of **26** and **27** (9.2 mg, 40% combined yield, 42:58 determined by ^{1}H NMR) from **18** (35.2 mg, 0.15 mmol), a mixture of **28** and **29** (9.7 mg, 44% combined yield, 44:56 determined by ^{1}H NMR) from **19** (30.6 mg, 0.10 mmol), a mixture of **31** and **32** (6.6 mg, 18% combined yield, 40:60 determined by ^{1}H NMR) from **24** (55.7 mg, 0.22 mmol), and a mixture of **33** and **34** (4.6 mg, 21% combined yield, 64:36 determined by ^{1}H NMR) from **25** (29.5 mg, 0.09 mmol).

Theoretical Calculation of 19 and 20. Geometries of **1**, **15**, and **3** were at first optimized by the semiempirical PM3 method. Geometry optimization at the *ab initio* 3-21G(*) level was then carried out using the PM3 optimized structures as the initial geometry.

Acknowledgment. We thank Mr. Odagaki (ONO Pharmaceutical Co., LTD) for X-ray analysis of **3**.

Supplementary Material Available: A listing of optimized geometries of **1**, **3**, and **15**, and ^{1}H and ^{13}C NMR spectra for all new compounds (51 pages). This material is contained 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.

JO9421283