© 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 3221—3233 (1984)

Diene-transmissive Diels-Alder Cycloaddition Reaction of Bis(silyloxy) Cross-conjugated Trienes

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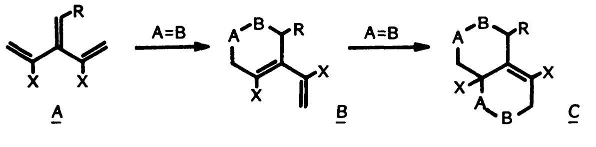
(Received June 18, 1984)

Multiple Diels-Alder reaction of bis(silyloxy) cross-conjugated trienes is presented. Two trienes, 3-benzylidene- and 3-(methoxymethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene, undergo two sequential Diels-Alder cycloadditions with a variety of dienophiles forming hydronaphthalene rings. Some characteristics of this reaction have been discussed in terms of stereo-, regio-, and chemoselectivity. It is proposed that this process is referred to as "diene-transmissive Diels-Alder reaction".

There have been reported numerous processes by which ring systems can be prepared. Although each has the characteristic advantages, one of the most reliable processes is the Diels-Alder cycloaddition that generally proceeds in a highly diastereoselective manner.[1] Recently a process that produces more than one ring in a single reaction has been often requested in elaborating complex natural products. Attracting is the use of the Diels-Alder reaction as a part of ring construction steps. Some examples are known for the multiple sequence of the Diels-Alder cycloaddition and called Domino,[2] Timed,[3] and Tandem Diels-Alder reaction.[4,5] However, their applications in organic synthesis are rare.

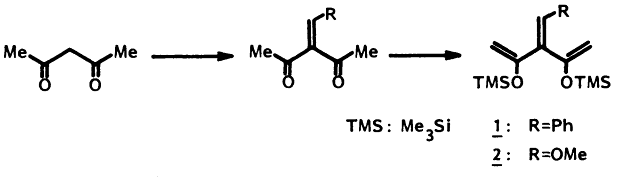
We have found a new process of multiple sequence of the Diels-Alder reaction. The process, referred to as "diene-transmissive Diels-Alder reaction",[6] involves two sequential cycloadditions of cross-conjugated triene: A part of the triene **A** undergoes the first cycloaddition to a dienophile (A=B) forming a six-membered ring **B** with an endocyclic double bond which serves as a part of diene for the following reaction. The second cycloaddition gives a bis-cycloadduct **C**. The cross-conjugated triene **A** of our choice carries two silyloxy moieties (X=OTMS, TMS: trimethylsilyl) as diene-activating and directing substituents.



The present paper describes the full detail of our investigation on the diene-transmissive Diels-Alder reactions of bis(silyloxy) cross-conjugated trienes, a part of which has been already reported as preliminary communications.[6—8]

Results and Discussion

Synthesis of Bis(silyloxy) Cross-conjugated Trienes. Blomquist[9] and Bailey[10] have reported the first examples of diene-transmissive Diels-Alder reaction using the parent cross-conjugated triene, 3-methylene-1,4-pentadiene. However, this elegant ring formation has long discouraged its application in organic synthesis because of tough handling, ready polymerization, low reactivity as a diene, and difficult structural modification of the triene. Our bis (silyloxy) cross-conjugated trienes can be synthesized in two steps from readily available 2,4-pentanedione, and a variety of substituents may be introduced from aldehydes.



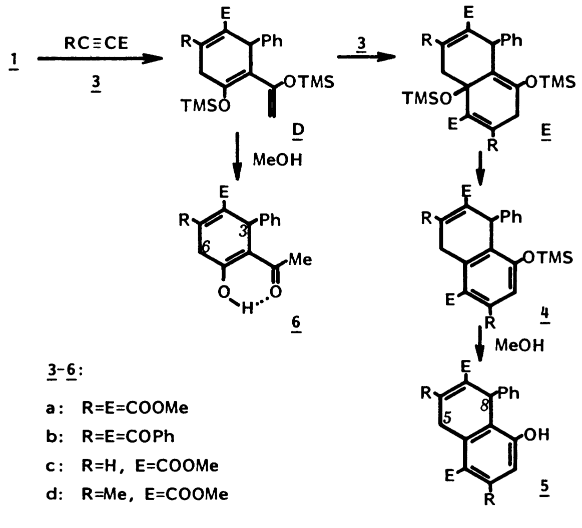
Scheme 1.

Scheme 1 illustrates the synthesis of trienes, 3-benzylidene- **1** and 3-(methoxymethylene)-2,4-bis(trimethyl silyloxy)-1,4-pentadiene **2**. The condensation products of 2,4-pentanedione with benzaldehyde and trimethyl orthoformate were silylated with chlorotrimethylsilane giving **1** and **2**. The use of 1,8-diazabicyclo-[5.4.0]undec-7-ene in dichloromethane[11] for **1** and of triethylamine together with a catalytic amount of zinc chloride in benzene[12] for **2** gave the best results.

The trienes **1** and **2** are stable enough to be purified by a vacuum distillation and chromatographed over silica gel if carefully handled.[13] In the absence of moisture, they may be stored for a long time without decomposition and polymerization.[14] Such thermal stability of **1** and **2** is a great advantage over the parent triene.

Cycloadditions to Acetylenic Dienophiles. The reaction of **1** with dimethyl acetylenedicarboxylate **3a** (five equiv) under reflux in benzene gave a desilylated bis-adduct **5a** after the usual work-up with methanol (Scheme 2 and Table 1). As shown in Scheme 2, the first Diels-Alder reaction between **1** and **3a** forms a mono-cycloadduct **D** that bears a diene functionality activated by two silyloxy moieties. The second reaction occurs smoothly affording a bis-cycloadduct **E**. Aromatization of the secondarily formed ring induces the elimination of trimethylsilanol leading to **4a**. On work-up with methanol, **4a** is desilylated into **5a**. As the diene function in **D** is highly activated by two silyloxy substituents, the second cycloaddition is even more accelerated than the first, only a trace of mono-adduct **6a** being formed.

The diene-transmissive Diels-Alder reaction of **1** with an unsymmetrical acetylene provides another advan-



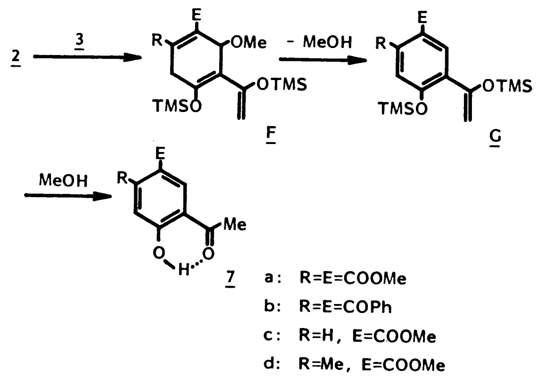
Scheme 2.

tage. The reaction with methyl propiolate **3c** gave bis-cycloadducts **4c** and **5c** besides a poor yield of mono-adduct **6c**, meaning that both the first and second cycloadditions proceeded in a highly regioselective manner. That is, the silyloxy groups in **1** serve not only as diene-activating substituents but also as directing ones.

Dibenzoylacetylene **3b** and methyl 2-butynoate **3d** failed in the formation either mono- or bis-adducts.

The other triene **2** was found much more reactive than **1**. It reacts with **3a** and **3b** even at room temperature, however the only products were mono-adducts **7a** and **7b** (Scheme 3 and Table 1). The exclusive formation of mono-adduct **7** from a reactive triene **2** remarkably contrasts with the predominant formation of bis-adduct **5** from a rather sluggish triene **1**. This is because of the ready elimination of methanol from the initially formed mono-cycloadduct **F**. ^{1}H-NMR spectral analysis of the reactions indicated that the methanol elimination occurred even at room temperature.

The triene **2** is a well designed conjugation system. Since it carries three alkoxyl groups, any two in a 1,3-relationship, both the first and second cycloadditions are highly accelerated and also regioselective. In addition, the methoxyl group is eliminated after the cycloaddition is complete, adding an unsaturation to the cycloadduct.



Scheme 3.

The reactions with **3c** and **3d**, under harder reaction conditions, provided regioselective mono-adducts **7c** and **7d**, respectively.

Cycloadditions to Cyclic Olefinic Dienophiles. To investigate the stereochemical aspect of diene-transmissive Diels-Alder reaction the cycloadditions with cyclic olefinic dienophiles were carried out.

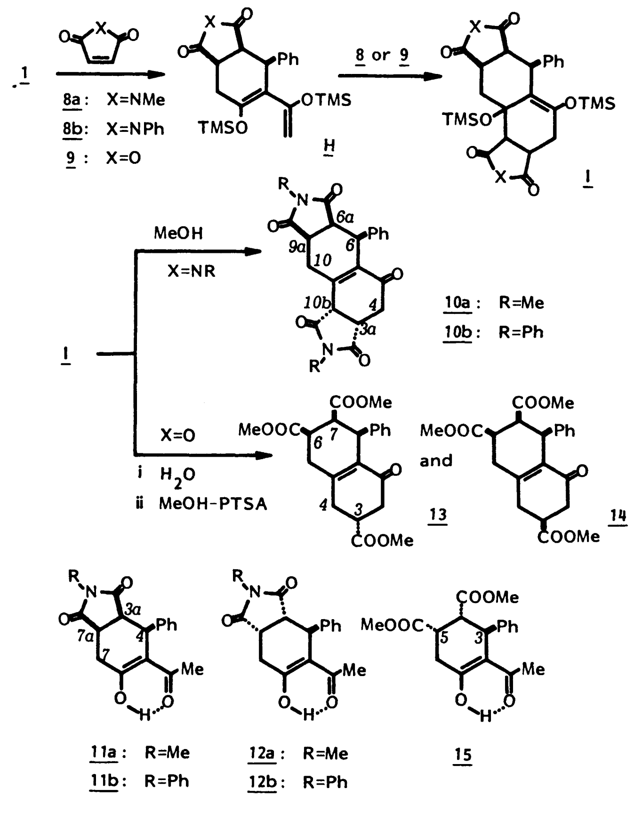
The reaction of **1** with excess of *N*-methylmaleimide **8a** under reflux in benzene and the work-up with methanol gave a bis-adduct **10a** together with low yields of two isomeric mono-adducts **11a** and **12a** (Scheme 4 and Table 2). The minor products were assigned as the 3a,4-*cis*- **11a** and 3a,4-*trans*-hydroisoindolinedione **12a**, respectively, on the basis of the spectral data, especially of the coupling constants between 3a-H and 4-H (**11a**: 6.0 Hz; **12a**: 2.0 Hz) as well as the chemical shifts of *N*-Me (**11a**: δ 2.38; **12a**: δ 3.00). The cis and trans mono-adducts correspond to the products derived through an endo and an exo approach of dienophile **8a** across the trans diene part of **1**, respectively.[15] In the present paper, therefore, the compound of type **11a** is to be called an endo adduct and **12a** an exo adduct.

Stereochemistry of the bis-adduct **10a** has been determined at two stages, the first Diels-Alder reaction (from **1** to the mono-cycloadduct) and the second reaction (the path to the second cycloadduct). Main path of the first cycloaddition should be endoselective since **11a** was only isolated in the reaction of **1** with **8a** at room temperature (Table 2). The ^{1}H-NMR spectrum con-

TABLE 1. REACTIONS OF **1** AND **2** WITH ACETYLENIC DIENOPHILES **3**

Triene	Acetylene (equiv)	Reaction Conditions			Product (yield/%)[a]	
		Solvent	Temp	Time/h	Bis-adduct	Mono-adduct
1	**3a** (5.0)	Benzene	Reflux	72	**5a** (51)	+
1	**3c** (3.0)	Toluene	110—5 °C[b]	140	**5c** (37)	+
1	**3c** (11.0)	Benzene	Reflux	168	**4c** (37), **5c** (10)	**6c** (2)
2	**3a** (2.0)	Benzene	r.t.	24	—	**7a** (57)
2	**3b** (2.0)	Benzene	r.t.	24	—	**7b** (47)
2	**3c** (2.0)	Benzene	Reflux	48	—	**7c** (35)
2	**3d** (2.0)	Toluene	Reflux	48	—	**7d** (8)

a) Isolated yields based on the trienes. The sign + (or —) means that adducts were (or were not) detected by ^{1}H-NMR spectroscopy. b) In a sealed tube.



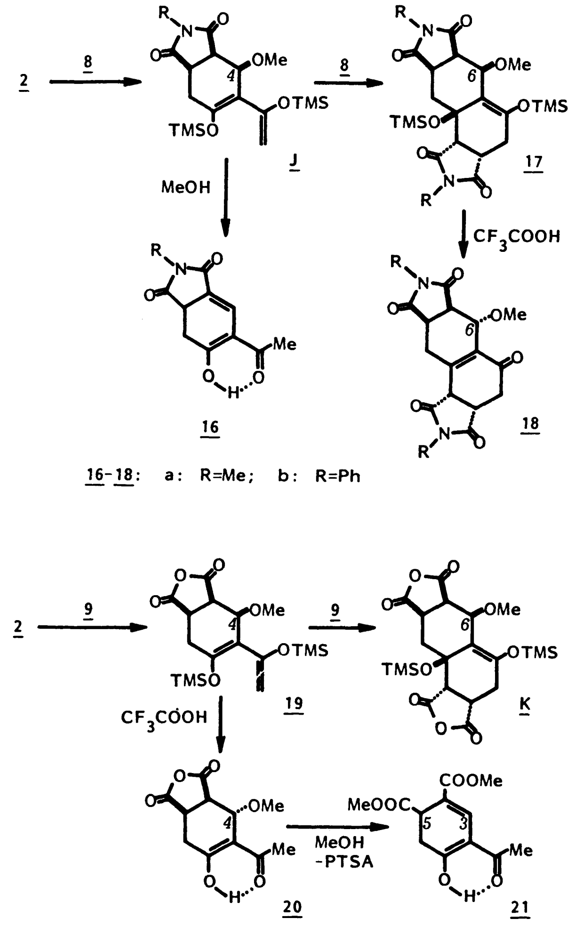
Scheme 4.

firmed cis configuration at the 6- and 6a-positions of **10a** (J_{6-6a}=6.0 Hz; *N*-Me: δ 2.33). Although the stereochemistry at the 3a- and 10b-junctions could not be determined only on the basis of the spectral data, it was tentatively assigned according to the probable reaction pathway shown in Scheme 4. The first cycloaddition of **1** to **8a** is highly endoselective leading to an endo monocycloadduct **H** (X=NMe). The second molecule of **8a** approaches across the diene conjugation of **H** in an endo fashion from the less hindered side (the opposite side of the fused maleimide ring and the phenyl) forming a stereoselective skeleton of bis-cycloadduct **I** (X=NMe). When treated with methanol, desilylation occurs to give a fused cyclohexenone ring **10a**.

Similar results were given in the reaction of **1** with *N*-phenylmaleimide **8b** as shown in Scheme 4 and Table 2.

Maleic anhydride **9** was found much more reactive than the maleimides. Triene **1** reacted with two equivalents of **9** under reflux in benzene forming **I** (X=O) as a major product, which was found composed of two isomers of bis-cycloadducts. The followed esterification with methanol in the presence of *p*-toluenesulfonic acid gave two isomeric decarboxylated bis-adducts **13** and **14** besides a small amount of exo mono-adduct **15**. Even with less than one equivalent of **9** at room temperature, **I** was only obtained in a good yield. It is surprising that the second cycloaddition of **9** has shown such a low stereoselectivity. The reason has not been clarified yet.

One of the four expected ester groups in the esterified bis-adducts was missing. It was eliminated during the hydrolysis of two anhydride rings in **I** (X=O). On the basis of the ^{1}H-NMR spectrum which showed no methylene multiplets upfield of δ 2.0,[16] it was confirmed that the lost carboxyl group had been at the 4-position. Among four positions (3-, 4-, 6-, and 7-positions), a carbanion that is expected to form on decarboxylation would be best stabilized at the 4-position.



Scheme 5.

The activated cross-conjugated triene **2** readily reacts with **8** and **9** under mild reaction conditions in a highly chemoselective manner. Type of products is dependent upon the amount of dienophile as well as the reaction conditions as shown in Scheme 5 and Table 2.

The reaction of **2** with an equivalent of **8a** in benzene at room temperature was followed by the work-up with methanol giving only a mono-adduct **16a** in a good yield. As **16a** was accompanied with the elimination of methanol, stereoselectivity in the first cycloaddition leading to a mono-cycloadduct **J** is not clear. With two equivalents of **8a** under reflux in benzene, a stereoselective bis-cycloadduct **17a** was isolated as the single product. Desilylation readily took place giving a bis-adduct **18a** when **17a** was treated with a catalytic amount of trifluoroacetic acid in benzene. Interesting is that the configuration at the 6-position of **17a** was inverted at the acid-catalyzed desilylation stage, probably through an elimination-addition mechanism.

As the structure of **17a** could not be determined only on the basis of spectral data, it was tentatively assigned by the following discussion: Molecular model inspection indicates that the most stable conformation for **J** is an envelope type in which a bulky substituent **R′** (=OMe) occupies an axial position in order to minimize the steric repulsion to the 3-carbonyl and the protruding silyloxy groups (Fig. 1). Although both sides of diene in the exo mono-cycloadduct exo-**J** as well as the upper side of the endo one endo-**J** are sterically hindered for the approach of **8a**, an endo approach from the bottom side of diene in endo-**J** looks quite easy. This approach must be the reaction leading to the stereoselective bis-cycloadduct **17a**. Thus, **17a** was assigned as a bis-cycloadduct formed via the endo mono-cycloadduct endo-**J**. On the other hand, the stereochemistry at the 6- and 6a-positions of **18a** was easily determined as trans on the basis of small J_{6-6a} (4.0 Hz) since this ring has an envelope conformation with an axial 6-methoxyl substituent.

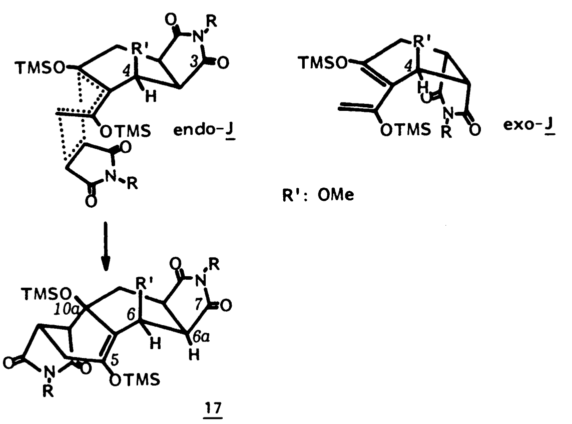


Fig. 1. Possible configuration and conformation for mono-cycloadduct **J**, and stereochemistry for second cycloaddition.

Similarly the stereoselective mono- **16b** and bis-adducts **17b** and **18b** were selectively formed in the reactions with *N*-phenylmaleimide **8b**. The stage of desilylation of **17b** into **18b** was also accompanied with the inversion of methoxyl moiety.

The reaction of **2** with an equivalent of maleic anhydride **9** was so rapid as to be completed in 10 min at room temperature forming a quantitative yield of endo mono-cycloadduct **19**. Treatment of **19** with trifluoroacetic acid in benzene provided a desilylated mono-adduct **20** while the usual work-up with methanol gave a mixture of two isomeric half esters. Esterification of **20** with methanol in the presence of *p*-toluenesulfonic acid led to a methanol eliminated mono-adduct **21** that was also obtained directly from **19** under the same conditions. Although the quantitative formation of a bis-cycloadduct **K** was confirmed in the reaction between **2** and two equivalents of **9**, neither its purification nor the conversion into isolable derivatives was successful.

To be emphasized are given as follows: 1) The first cycloaddition of both **1** and **2** is highly endoselective and the second reaction selectively takes place with an endo approach of dienophiles from the less hindered side of diene moiety. 2) The double cycloaddition sequence of **2** is highly chemoselective. Either the mono- or bis-cycloadduct is selectively formed depending upon the amount of dienophiles. 3) The elimination of methanol in the reactions of **2** adds an unsaturation to the products.

Cycloadditions to Acyclic Olefinic Dienophiles. Compared with such highly reactive dienophiles as **3**, **8**, and **9**, acyclic olefinic dienophiles show a low reactivity toward the trienes **1** and **2**. The first cycloaddition slowly proceeds with a poor stereoselec-

Table 2. Reactions of 1 and 2 with cyclic olefinic dienophiles 8 and 9

Triene	Olefin (equiv)	Reaction Conditions[a]		Product (yield/%)[b]	
		Temp	Time/h	Bis-adduct	Mono-adduct
1	**8a** (2.3)	r.t.	48		**11a** (23)
1	**8a** (3.0)	Reflux	72	**10a** (60)	**11a** (2), **12a** (3)
1	**8b** (2.0)	r.t.	120	**10b** (13)	**11b** (26)
1	**8b** (3.0)	Reflux	48	**10b** (80)	**11b** (3), **12b** (6)
1	**9** (2.0)	Reflux	48	**13** (57), **14** (22)	**15** (7)
1	**9** (2.0)	Reflux	48	**I** (82)[c]	—
1	**9** (0.75)	r.t.	72	**I** (63)[d]	—
2	**8a** (1.0)	r.t.	24	—	**16a** (64)
2	**8a** (2.0)	Reflux	24	**17a** (63)	—
2	**8b** (1.0)	50 °C	20	—	**16b** (73)
2	**8b** (2.0)	Reflux	20	**17b** (62)[e]	—
2	**9** (1.0)	r.t.[f]	0.2	—	**19** (100)[g]
2	**9** (1.0)	r.t.[f]	0.2	—	**21** (56)
2	**9** (2.0)	r.t.	4	**K** (100)[h]	

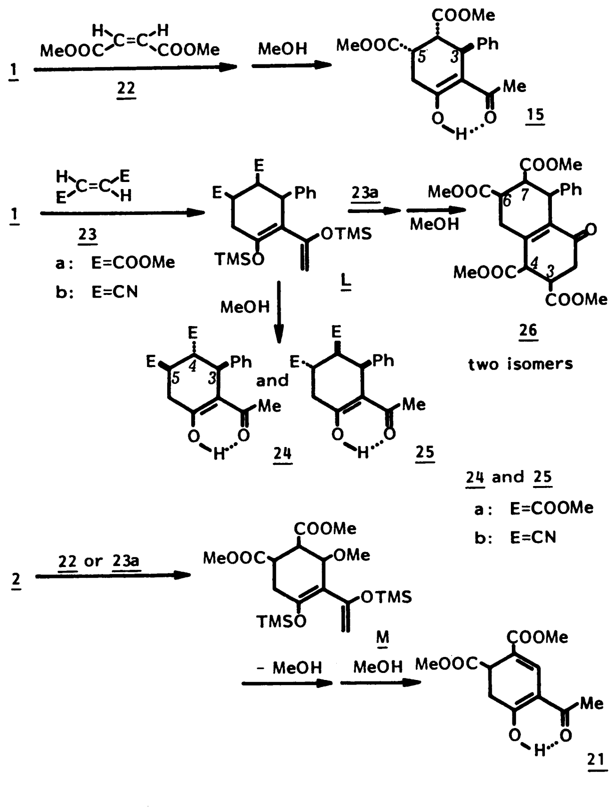
a) All the reactions were carried out in dry benzene. b) Isolated yields based on the trienes. c) Isomer ratio = 2.5 : 1. d) Isomer ratio = 3 : 1. e) Together with an unidentified bis-adduct (9%). f) Without solvent. g) Determined by ^{1}H-NMR spectroscopy. h) Determined by ^{1}H-NMR spectroscopy. Its isolation failed.

tivity, a mixture of endo and exo mono-cycloadducts being formed in a comparable ratio. Regardless of the stereochemistry of mono-cycloadduct, the second cycloaddition is extremely slow probably because the initially formed six-membered ring takes a half-chair conformation which is hardly favored for the approach of the second molecule of dienophile. Therefore, the major products in the diene-transmissive Diels-Alder reactions with acyclic olefinic dienophiles are mono-adducts.

The reaction of **1** with dimethyl maleate **22** (large excess) gave an exo mono-adduct **15** that was identical with the minor product in the reaction of **1** with **9** (Scheme 6 and Table 3). On the other hand, with dimethyl fumarate **23a** under the same reaction conditions, an exo- **24a** and an endo mono-adduct **25a** were obtained together with a mixture of two isomeric bis-adducts **26**. In this case also the exo adduct **24a** was the major product. When the same reaction was carried out under harder conditions (under reflux in toluene), the yield of **26** increased up to 88% and those of both **24a** and **25a** decreased. These results indicate that two isomers of bis-adducts **26** carry different stereochemistry in the initially formed ring, and further indicate that both the endo and exo mono-cycloadducts **L** can undergo the second cycloaddition with a comparable easiness.

The most stable conformation for the six-membered rings of **15**, **24a**, and **25a** is a half-chair type.[17] Molecular model inspection shows that the bulky phenyl substituent at the 3-position occupies an axial position to avoid the steric hindrance to the adjacent acetyl moiety. Consequently an axial substituent at the 5-position, which is in a 1,3-relationship to the phenyl, faces closely to the phenyl plane and therefore is magnetically shielded. Thus the isomer with a shielded ester group (COOMe: δ 3.32) was assigned to **24a**, and then the other **25a**.

Two conformers of the exemplified compound **14** are illustrated in Fig. 2. It is clear that not the adjacent but the next ester is most intensely shielded when it is sitting cis to the axial phenyl. The following six compounds give good examples for the chemical shifts of a variety of ester methyls and the coupling constants J_{3-4} of cyclohexene ring systems of related compounds. These values agree with the ones estimated on the axial-phenyl conformation model.



Scheme 6.

Table 3. Reactions of **1** and **2** with acyclic dienophiles **22**, **23**, and **27**

Triene	Olefin (equiv)	Reaction Conditions			Product (yield/%)[a]	
		Solvent	Temp	Time/h	Bis-adduct	Mono-adduct
1	**22** (6.3)	Benzene	Reflux	7 d		**15** (45)
1	**23a** (3.0)	Benzene	Reflux	7 d	**26** (25)[b]	**24a** (55), **25a** (11)
1	**23a** (2.2)	Toluene	Reflux	7 d	**26** (88)[b]	**24a** (10), **25a** (2)
1	**23b** (3.0)	Toluene	Reflux	7 d		**24b** (10)[c], **15b** (55)
2	**22** (1.0)	Benzene	Reflux	48		**21** (42)
2	**22** (3.0)	Benzene	Reflux	72		**M** (100)[d]
2	**23a** (1.0)	Benzene	Reflux	48		**21** (82)
1	**27a** (20)	Benzene	Reflux	6 d		**28a** (48), **29a** (20)
1	**27b** (20)	Benzene	Reflux	5 d		**28b** (70), **29b** (22)
1	**27c** (e)	**27c**	Reflux	58		**28c** (54), **29c** (18)
1	**27c** (e)	Benzene	110 °C[f]	5 d	**30** (38)[b]	**28c** (27), **29c** (6)
2	**27a** (5.0)	Benzene	Reflux	48		**31a** (60)
2	**27b** (3.0)	Benzene	Reflux	48		**31b** (66)
2	**27c** (5.0)	Benzene	75 °C	48		**31c** (73)

a) Isolated yields based on the trienes. b) Mixtures of two isomers. c) Determined by ^{1}H-NMR. d) The structure was assigned as exo mono-cycloadduct on the basis of ^{1}H-NMR spectrum. e) The dienophile was also used as the solvent. f) In a sealed tube.

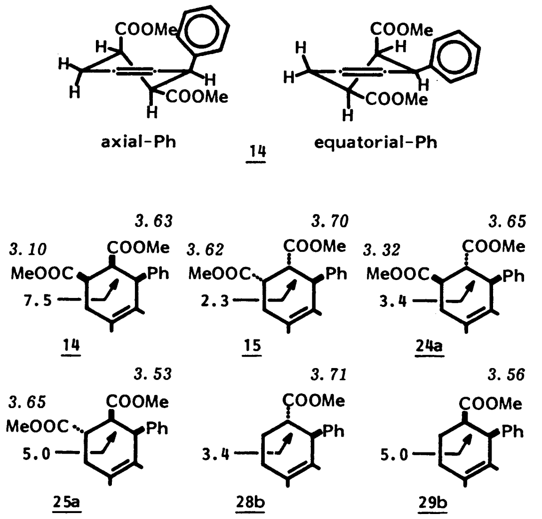


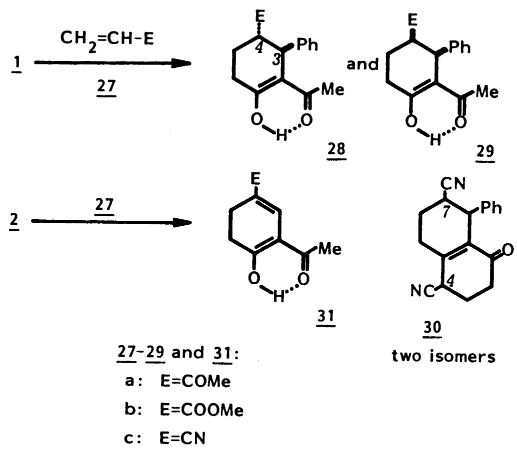
Fig. 2. Two half-chair conformations for **14**, and chemical shifts (δ ppm) of ester methyls and coupling constants (Hz) between 3-H and 4-H of related cyclohexene ring systems.

Fumaronitrile **23b** also reacted with **1** under reflux in toluene giving a mixture of two isomeric mono-adducts **24b** and **25b**, but in this case the endo adduct **25b** was the major product.

The same methanol-eliminated mono-adduct **21** was yielded both in the reaction of **2** with the fumarate **22** and in that with the maleate **23a**. As have been shown in Scheme 5, this compound **21** is also obtainable from **2** and maleic anhydride **9**. In the prolonged reaction with excess of **22**, a quantitative formation of exo mono-cycloadduct **M** was confirmed by ^{1}H-NMR spectroscopy, no trace of either bis-adduct or endo mono-adduct being formed. These results indicate that the reaction of activated triene **2** with **22** takes place in a highly chemoselective (selective mono-cycloadduct formation) and exoselective manner, and that the methanol elimination occurs only after the desilylation. When the cycloadduct **M** was treated with methanol, **21** was obtained in a good yield.

Both trienes **1** and **2** reacted with unsymmetrical olefinic dienophiles such as methyl vinyl ketone **27a**, methyl acrylate **27b**, and acrylonitrile **27c** in a highly regioselective manner, but its stereoselectivity was low. So far as these reactions were carried out around 80 °C, only the mono-adducts were afforded.

Even with large excess of **27**, the reactions of **1** under reflux in benzene or in a dienophile itself (**27c**) gave only the mono-adducts as mixtures of exo **28** and endo isomers **29** (Scheme 7 and Table 3). In all cases, the exo isomers were the major products. Their structures were based on the chemical shifts of substituents at the 4-position as well as the coupling constants between 3-H and 4-H. When the reaction with **27c** was carried out under harder conditions (at 110 °C in a shield tube for 5 d), a mixture of two isomeric bis-adducts **30** was obtained in a fair yield. They are the isomers which have different configurations in the initially formed six-membered ring.



Scheme 7.

In the similar reactions of **2** with **27**, the only obtained products were the regioselective mono-adducts **31**. These products were also accompanied with methanol elimination, the stereochemical selectivity of mono-cycloadduct formation being ambiguous.

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus and uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-102 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-40 or a JEOL FX-100 instrument and ^{13}C-NMR spectra were obtained on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer at 75 eV of ionization energy. Elementary analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or on 0.2 mm precoated plates of aluminum oxide 60 F-254 type E (Merck). Visualization was with ultraviolet light (254 and 365 nm) and iodine. Wakogel C200 and C300 (Wako) were used for preparative column chromatography. Preparative high performance liquid chromatography (HPLC) was carried out on a Kusano KHLC-201 apparatus with a UV-detector Uvilog-III using a column (22×300 mm) packed with silica gel (Wakogel LC-50H). Micro vacuum distillation was performed with a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type V at about 50 °C unless otherwise stated.

Benzene and toluene were purified by the distillation of the predried commercial solvents and stored on sodium wire. Dichloromethane was dried on calcium chloride and then distilled on calcium hydride.

Materials. 3-Benzylidene-[18] and 3-(methoxymethylene)-2,4-pentanedione[19] were prepared by the condensations of 2,4-pentanedione with benzaldehyde in the presence of piperidine and with trimethyl orthoformate in the presence of acetic anhydride, respectively. Dibenzoylacetylene **3b**[20] was synthesized from the bromination and dehydrobromination procedure of *trans*-1,2-dibenzoyl-ethene. Methyl propiolate **3c**[21] and 2-butynoate **3d** were obtained by the esterification of the corresponding acids with methanol in the presence of *p*-toluenesulfonic acid. Propynoic acid was commercially available and 2-butynoic acid[22] was prepared by the reaction of propyne with butyllithium and then with carbon dioxide.

As for the following reagents, the ones of commercial grade were purified by distillation or crystallization: Triethylamine: distilled on potassium hydroxide and stored on the same agent; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU): distilled and stored on molecular sieves 5A; zinc chloride: crystallized from anhydrous dioxane and dried over phosphorus pentaoxide under vacuum; dimethyl acetylenedicarboxylate **3a**, methyl vinyl ketone **27a**, methyl acrylate **27b**, and acrylonitrile **27c**: distilled; maleic anhydride **9**: distilled under vacuum and stored in a bottle with a tightly-fitting stopper. The other reagents were all commercially available and no further purification was needed.

3-Benzylidene-2,4-bis(trimethylsilyloxy)-1,4-pentadiene 1. To a mixture of 3-benzylidene-2,4-pentanedione (9.41 g, 0.1 mol) and DBU (15.22 g, 0.1 mol) in dry dichloromethane (25 ml) was added chlorotrimethylsilane (13.9 ml, 0.11 mol) at room temperature. The mixture was heated at 40 °C under dry atmosphere for 20 h and then all the volatile materials were removed *in vacuo*. The residue was triturated with dry hexane (100 ml) and the hexane separated from the insoluble DBU · HCl was concentrated *in vacuo* to give 15.05 g (91%) of crude **1**. This crude triene **1** was purified by a column chromatography over silica gel (Wako C200) using a mixture of benzene–hexane (1:9) as an eluent affording pure **1** (9.45 g, 57%) as a colorless liquid: bp 115 °C (107 Pa) (bulb-to-bulb); IR (neat) 1625, 1595 (C=C), 1245, and 830 cm^{-1} (TMS); ^{1}H-NMR (CCl$_4$) δ=0.17, 0.27 (each 9H, s, TMS), 4.17, 4.38 (each 1H, d, J=1.0 Hz, 1- and/or 5-CH$_2$), 4.35, 4.69 (each 1H, dd, J=1.0 and 0.6 Hz, 1- and/or 5-CH$_2$), 6.72 (1H, t, J=0.6 Hz, phC$\underline{\mathrm{H}}$=), and 7.00—7.46 (5H, m, ArH); ^{13}C-NMR (CCl$_4$) δ=0.00, 0.10 (each q, TMS), 94.83, 95.95 (each t, 1- and 5-C), 153.06, and 155.30 (each s, 2- and 4-C); MS m/z (rel. intensity) 332 (M$^+$; base peak), 241 (M$^+$—92, 25) and 73 (TMS$^+$, 79).

Found: C, 64.74; H, 8.60%; M$^+$, 332. Calcd for $C_{18}H_{28}O_2Si_2$: C, 65.00; H, 8.49%; M, 332.

Another procedure for **1** was briefly presented in the preceding communication.[6]

3-(Methoxymethylene)-2,4-bis(trimethylsilyloxy)-1,4-pentadiene 2. A mixture of dry zinc chloride (0.57 g) and triethylamine (31.17 g, 0.31 mol) was vigorously stirred at room temperature for 1 h and mixed with a solution of 3-(methoxymethylene)-2,4-pentanedione (9.95 g, 0.07 mol) and chlorotrimethylsilane (35.5 ml, 0.28 mol) in dry benzene (50 ml). The resultant mixture was heated at 40 °C for 24 h and cooled to room temperature. The salt precipitated was filtered off and the filtrate was concentrated *in vacuo* to afford a yellow residue. Vacuum distillation of the residue gave 16.44 g (82%) of triene **2** as colorless liquid: bp 72 °C (240 pa); IR (neat) 1685—1600 (C=C), 1250, and 840 cm^{-1} (TMS); ^{1}H-NMR (CDCl$_3$) δ=0.18, 0.23 (each 9H, s, TMS), 3.65 (3H, s, OMe), 4.13, 4.26, 4.40, 4.49 (each 1H, s, =CH$_2$), and 6.40 (1H, s, $\underline{\mathrm{C}}$HOMe); ^{13}C-NMR (CDCl$_3$) δ=0.15, 0.24 (each q, TMS), 60.47 (q, OMe), 91.52, 97.27 (each t, =CH$_2$), 117.34 (s, 3-C), 145.38 (d, $\underline{\mathrm{C}}$HOMe), 150.92, and 153.79 (each s, 2- and 4-C); MS m/z 286 (M$^+$), 271 (M$^+$—15, base peak), 147, 63, and 45.

Found: m/z 286.1435. Calcd for $C_{13}H_{26}O_3Si_2$: M, 286.1420.

Cycloaddition of 1 to 3a Leading to 5a. A mixture of freshly distilled **1** (0.64 g, 1.92 mmol) and **3a** (1.37 g, 9.6 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 72 h, the benzene was evaporated *in vacuo*, and the residue was treated with methanol (10 ml) at room temperature overnight. The methanol was completely removed off *in vacuo* to give a viscous oil which was then chromatographed over silica gel using chloroform–hexane (1:1) as an eluent. Crude **5a** (0.438 g, 51%) was purified by crystallization from ether–hexane.

5a: Colorless prisms; mp 171—173 °C; IR (KBr) 3360 (OH), 1725, 1715, 1665 (C=O), 1590, 1280, and 1245 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=3.64 (1H, dd, J_{5-8}=2.8 and J_{gem}=21.8 Hz, one of 5-CH$_2$), 3.64, 3.74, 3.76, 3.89 (each 3H, s, COOMe), 3.95 (1H, dd, J_{5-8}=4.0 and J_{gem}=21.8 Hz, the other of 5-CH$_2$), 5.30 (1H, dd, 8-H), and 7.04—7.16 (6H, m, ArH and 2-H); ^{13}C-NMR (CDCl$_3$) δ=29.12 (t, 5-C), 42.08 (d, 8-C), 52.55, 52.80 (each q, COO$\underline{\mathrm{Me}}$), 114.78 (d, 2-C), 153.99 (s, 1-C), 166.27, 167.74, 168.15, and 169.43 (each s, $\underline{\mathrm{C}}$OOMe); MS m/z (rel. intensity) 454 (M$^+$, 10), 423 (M$^+$—31, 39), 422 (M$^+$—32, 75), 363 (79), 345 (base peak), 313 (11), 304 (16), and 189 (10).

Found: C, 63.15; H, 4.98%; M$^+$, 454. Calcd for $C_{24}H_{22}O_9$: C, 63.43; H, 4.88%; M, 454.

Cycloaddition of 1 to 3c Leading to 4c, 5c, and 6c. A mixture of **1** (0.685 g, 2.06 mmol) and **3c** (2.0 g, 23.8 mmol), both freshly distilled, in dry benzene (3 ml) was refluxed under nitrogen for 168 h. When all the volatile materials were removed off *in vacuo* and the residue was treated with methanol (10 ml), colorless solid of **4c** (0.313 g, 37%) was precipitated. The methanol filtrate was stirred at room temperature overnight and then evaporated *in vacuo*. The viscous oil obtained was chromatographed over silica gel with chloroform–hexane (1:1) to give **5c** (0.07 g, 10%) and **6c** (0.01 g, 2%). Repeated chromatography provided a pure sample of **4c**; **5c** was purified by crystallization from ether–hexane to give colorless prisms; **6c** was distilled on a micro distillation apparatus.

4c: Colorless solid; mp 143—145 °C; IR (KBr) 1720, 1700 (C=O), 1250, 875, and 840 cm^{-1} (TMS); ^{1}H-NMR (CDCl$_3$) δ=0.13 (9H, s, TMS), 3.67, 3.83 (each 3H, s, COOMe), 4.09 (1H, dt, J_{5-6}=J_{5-8}=3.3 and J_{gem}=22.5 Hz, one of 5-CH$_2$), 4.15 (1H, ddd, J_{5-6}=5.2, J_{5-8}=2.6, and J_{gem}=22.5 Hz, the other of 5-CH$_2$), 5.30 (1H, dd, 8-H), 6.62 (1H, d, J_{2-3}=8.5 Hz, 2-H), 7.00—7.30 (6H, m, ArH and 6-H), and 7.76 (1H, d, 3-H); ^{13}C-NMR (CDCl$_3$) δ=0.00 (q, TMS), 30.41 (t, 5-C), 39.69 (d, 8-C), 51.25 (q, COO$\underline{\mathrm{Me}}$), 115.43 (d, 2-C), 120.77 (s, 4-C), 135.80 (d, 6-C), 156.34 (s, 1-C), 166.03, and 167.14 (each s, $\underline{\mathrm{C}}$OOMe); MS m/z (rel. intensity) 411 (M$^+$+1, 30), 410 (M$^+$, base peak), 379 (15), 378 (13), 351 (16), 334 (17), 333 (68), 301 (43), and 73 (40).

Found: C, 67.41; H, 6.44%; M$^+$, 410. Calcd for $C_{23}H_{26}O_5Si$: C, 67.29; H, 6.38%; M, 410.

5c: Colorless prisms (from ether–hexane); mp 179—181 °C; IR (KBr) 3230 (OH), 1720—1660 (C=O), 1575, 1250, and 1225 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=3.67, 3.84 (each 3H, s, COOMe), 4.08 (1H, dt, J_{5-6}=J_{5-8}=3.2 and J_{gem}=23.0 Hz, one of 5-CH$_2$), 4.15 (1H, ddd, J_{5-6}=5.2, J_{5-8}=2.6, and J_{gem}=23.0 Hz, the other of 5-CH$_2$), 5.41 (1H, dd, 8-H), 6.60 (1H, d, J_{2-3}=8.5 Hz, 2-H), 7.00—7.34 (6H, m, ArH and 6-H), and 7.76 (1H, d, 3-H); ^{13}C-NMR (CDCl$_3$) δ=30.65 (t, 5-C), 39.39 (d, 8-C), 51.78 (q, COO$\underline{\mathrm{Me}}$), 113.31 (d, 2-C), 120.30 (s, 4-C), 136.85 (d, 6-C), 157.04 (s, 1-C), 166.85, and 167.73 (each s, $\underline{\mathrm{C}}$OOMe); MS m/z (rel. intensity) 339 (M$^+$+1, 19), 338 (M$^+$, 83), 307 (M$^+$—31, 23), 306 (M$^+$—32, 20), 279 (21), 278 (32), 261 (64), 260 (31), 247 (64), 229 (base peak), 191 (25), 189 (41) and 115 (21).

Found: C, 70.93; H, 5.39%; M$^+$, 338. Calcd for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36%; M, 338.

6c: Colorless viscous liquid; bp 120 °C (200 Pa) (bulb-to-bulb); IR (neat) 3400 (OH), 1720, 1660 (C=O), 1600, and 1245 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.05 (3H, s, COMe), 3.27 (1H, ddd, J_{6-3}=3.0, J_{6-5}=4.8, and J_{gem}=22.0 Hz, one of 6-CH$_2$), 3.37 (1H, ddd, J_{6-5}=3.2, J_{6-3}=3.7, J_{gem}=22.0 Hz, the other of 6-CH$_2$), 3.68 (3H, s, COOMe), 4.83 (1H, dd, 3-H), 6.83 (1H, dd, 5-H), 7.10-7.24 (5H, br. s, ArH), and 15.96 (1H, br. s, OH); ^{13}C-NMR (CDCl$_3$) δ=25.60 (t, 6-C), 32.58 (1, CO$\underline{\mathrm{Me}}$), 41.80 (d, 3-C), 51.72 (q, COO$\underline{\mathrm{Me}}$), 109.56 (s, 2-C), 165.68 (s, $\underline{\mathrm{C}}$OOMe), 177.89 (s, $\underline{\mathrm{C}}$OMe), and 199.20 (s, 1-CO); MS m/z (rel. intensity) 273 (M$^+$+1, 17), 272 (M$^+$, base peak), 254 (M$^+$—18, 34), 222 (22), 213 (31), 197 (29), 195 (34), 129 (40), and 128 (17).

Found: C, 70.45; H, 6.08%; M$^+$, 272. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%; M, 272.

Cycloaddition of 2 to 3a Leading to 7a. A solution of **2** (0.85 g, 3.0 mmol) and **3a** (0.843 g, 6.0 mmol), both freshly distilled, in dry benzene (4 ml) was stirred at room temperature under nitrogen for 24 h. After evaporation of all the volatile materials, the residue was treated with methanol (10 ml) at room temperature overnight. The methanol was completely evaporated *in vacuo* to give a residue which was then chromatographed over silica gel using chloroform–ethyl acetate (3:1) as an eluent. Colorless needles (from aqueous methanol) of **7a** (0.425 g, 57%) were obtained:

7a: Colorless needles from aqueous methanol; mp 77 °C; IR (KBr) 1720 and 1645 cm^{-1} (C=O); ^{1}H—NMR (CDCl$_3$) δ= 2.67 (3H, s, MeCO), 3.87, 3.90 (each 3H, s, COOMe), 7.02 (1H, s, 6-H), 8.27 (1H, s, 3-H), and 12.50 (1H, s, OH); MS *m/z* 252 (M$^+$), 237 (M$^+$−15), and 221 (M$^+$−31, base peak).

Found: C, 56.93; H, 4.87%; M$^+$, 252. Calcd for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80%; M, 252.

Cycloaddition of 2 to 3b Leading to 7b. Similar reaction between **2** (0.547 g, 1.9 mmol) and **3b** (0.447 g, 1.9 mmol) in 3 ml of benzene under the conditions shown in Table 1 gave 0.31 g (47%) of **7b** which was precipitated on the work-up with methanol.

7b: Colorless leaflets from dichloromethane–methanol; mp 189-190 °C; IR (KBr) 1670—1640 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.60 (3H, s, COMe), 7.07 (1H, s, 6-H), 7.20—7.70 (10H, m, ArH), 8.02 (1H, s, 3-H), and 12.60 (1H, s, OH); MS *m/z* 344 (M$^+$) and 267 (M$^+$−77, base peak).

Found: C, 76.47; H, 4.75%; M$^+$, 344. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%; M, 344.

Cycloaddition of 2 to 3c Leading to 7c. Similar reaction starting from **2** (0.573 g, 2.0 mmol) and **3c** (0.336 g, 4.0 mmol) under the conditions shown in Table 1 gave 0.134 g (35%) of **7c**, after a chromatography over silica gel with chloroform.

7c: Colorless needles from aqueous methanol; mp 99—99.5 °C; IR (KBr) 1720 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.68 (3H, s, COMe), 3.90 (3H, s, COOMe), 6.96 (1H, d, J_{6-5}=9.0 Hz, 6-H), 8.06 (1H, dd, J=9.0 and 2.0 Hz, 5-H), 8.42 (1H, d, J= 2.0 Hz, 3-H), and 12.60 (1H, s, OH); MS *m/z* 194 (M$^+$) and 179 (M$^+$−15, base peak).

Found: C, 62.09; H, 5.14%; M$^+$, 194. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%, M, 194.

Cycloaddition of 2 to 3d Leading to 7d. Similar reaction between **2** (0.886 g, 3.1 mmol) and **3d** (0.607 g, 6.2 mmol) under the conditions of Table 1 gave 0.045 g (8%) of **7d**, after a chromatography over silica gel with chloroform.

7d: Colorless needles from aqueous methanol; mp 70 °C; IR (KBr) 1720 and 1635 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.60 (3H, s, 5-Me), 2.64 (3H, s, COMe), 3.87 (3H, s, COOMe), 6.77 (1H, s, 6-H), 8.36 (1H, s, 3-H), and 12.42 (1H, s, OH); MS *m/z* 208 (M$^+$) and 193 (M$^+$−15, base peak).

Found: 63.17; H, 5.99%; M$^+$, 208. Calcd for $C_{11}H_{10}O_4$: C, 63.45; H, 5.81%; M, 208.

Cycloaddition of 1 to 8a Leading to 10a, 11a, and 12a. A solution of **1** (0.43 g, 1.29 mmol) and **8a** (0.333 g, 3.0 mmol) in dry benzene (1.5 ml) was stirred at room temperature under nitrogen for 48 h. The benzene was evaporated *in vacuo* and the residue was treated with methanol (10 ml) at room temperature overnight. The methanol was removed *in vacuo* to afford a viscous residue, it was treated with water, extracted with chloroform, the chloroform was dried over magnesium sulfate, and finally evaporated *in vacuo*. Trituration of the viscous oil obtained with ether–hexane gave 0.089 g (23%) of **11a**.

11a: Colorless prisms from ether–hexane; mp 163—165 °C; IR (KBr) 1775, 1700 (C=O), and 1610 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.04 (3H, s, COMe), 2.38 (3H, s, NMe), 2.80 (1H, dd, J_{gem}=21.0 and J_{7-7a}=12.5 Hz, one of 7-CH$_2$), 3.00—3.45 (3H, m, the other of 7-CH$_2$, 3a-, and 7a-H), 4.38 (1H, d, J_{4-3a}=6.0 Hz, 4-H), and 6.80—7.30 (5H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=24.07 (7-C), 24.54 (NMe), 27.53 (COMe), 37.05, 41.33 (3a- and 7a-C), 46.15 (4-C), 108.38 (5-C), 127.99, 128.40, 128.69, 137.20, 176.84 (CON-), 178.01 (CON-), 182.71 (COMe), and 197.03 (6-C); MS *m/z* (rel. intensity) 299 (M$^+$, 27), 281 (25), 256 (19), 131 (22), 126 (30), 115 (26), and 77 (22).

Found: C, 68.37; H, 5.80; N, 4.63%; M$^+$, 299. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68%; M, 299.

A solution of **1** (0.475 g, 1.43 mmol) and **8a** (0.477 g, 4.29 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 72 h. The benzene was evaporated *in vacuo* to give a residue which solidified on treatment with methanol (15 ml). This colorless solid of **10a** (0.21 g) was collected on a filter and washed with another 5 ml of methanol. The combined methanol filtrate was stirred at room temperature overnight, evaporated *in vacuo*, and the residue obtained was chromatographed over silica gel. The fraction with chloroform–hexane (2:1) gave 0.055 g of mixture between **11a** (2%) and **12a** (3%), from which only **12a** was isolated by crystallization from ether–hexane. The fraction with chloroform–ethyl acetate 19:1 afforded 0.14 g of **10a**. Total amount of **10a** was 0.35 g (60%).

10a: Colorless prisms from benzene–hexane; mp 213—215 °C; IR (KBr) 1760, 1675 (C=O), and 1420 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.33 (3H, s, NMe), 2.53 (1H, dd, J_{gem}=17.0 and J_{10-9a}=9.0 Hz, one of 10-CH$_2$), 2.95 (1H, dd, J_{gem}=17.0 and J_{10-9a}=4.5 Hz, the other of 10-CH$_2$), 3.04 (3H, s, NMe), 3.20—3.75 (5H, m, 4-CH$_2$, 3a-, 6a-, and 9a-H), 3.92 (1H, d, J_{10b-3a}=8.0 Hz, 10b-H), 4.70 (1H, dd, J_{6-6a}=6.0 and J_{6-9a}=2.0 Hz, 6-H), and 6.70—7.22 (5H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=23.90 (t, 10-C), 25.36, 25.48 (each q, NMe), 34.64 (t, 4-C), 36.99, 38.34 (each d, 3a-, 6a-, and 9a-C), 44.09 (d, 10b-C), 44.50 (d, 6-C), 127.75 (d), 128.46 (d), 135.80 (s), 136.27 (s), 146.13 (s), 174.37, 176.66, 178.59 (each s, CON-), and 190.98 (s, 5-CO); MS *m/z* (rel. intensity) 393 (M$^+$+1, 33), 392 (M$^+$, base peak), 374 (59), 289 (35), 280 (29), 203 (25), 178 (28), 167 (22), 165 (28), and 115 (25).

Found: C, 67.59; H, 5.25; N, 7.14%; M$^+$, 392. Calcd for $C_{22}H_{20}N_2O_5$: C, 67.33; H, 5.14; N, 7.14%; M, 392.

12a: Colorless solid from ether–hexane; mp 126—128 °C; IR (KBr) 3420 (OH) and 1690 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.11 (3H, s, COMe), 2.54 (1H, dd, J_{gem}=19.5 and J_{7-7a}= 9.0 Hz, one of 7-CH$_2$), 2.76 (1H, dd, J_{gem}=19.5 and J_{7-7a}=2.3 Hz, the other of 7-CH$_2$), 3.00 (3H, s, NMe), 3.19 (1H, dt, J_{7a-7}=J_{7a-3a}=9.0 and J_{7a-7}=2.3 Hz, 7a-H), 3.60 (1H, dd, J_{3a-7a}=9.0 and J_{3a-4}=2.0 Hz, 3a-H), 4.68 (1H, d, J_{4-3a}=2.0 Hz, 4-H), and 7.04—7.43 (5H, m, ArH); MS *m/z* (rel. intensity) 300 (M$^+$+1, 17), 299 (M$^+$, 87), 281 (base peak), 170 (32), 142 (28), and 126 (42).

Found: C, 68.37; H, 5.79; N, 4.80%; M$^+$, 299. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68%; M, 299.

Cycloaddition of 1 to 8b Leading to 10b, 11b, and 12b. A solution of **1** (0.665 g, 2.0 mmol) and **8b** (0.692 g, 4.0 mmol) in 6 ml of dry benzene was stirred at room temperature under nitrogen for 120 h. The benzene was evaporated *in vacuo* and the residue was treated with methanol (15 ml) overnight to precipitate 0.18 g (26%) of **11b** which was collected and washed with another portion (5 ml) of methanol. The combined methanol filtrate was evaporated *in vacuo* and the viscous oil obtained was triturated with ether to give 0.135 g (13%) of **10b**.

10b: Colorless solid from chloroform–hexane; mp 278—280 °C; IR (KBr) 1770, 1700 (C=O), 1585, 1375, and 1175 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.63 (1H, dd, J_{gem}=16.5 and J_{10-9a}=9.0 Hz, one of 10-CH$_2$), 3.05 (1H, dd, J_{gem}=16.5 and J_{10-9a}=5.5 Hz, the other of 10-CH$_2$), 3.20—3.85 (5H, m, 4-CH$_2$, 3a-, 6a-, and 9a-H), 3.96 (1H, d, J_{10b-3a}=8.0 Hz, 10b-H), 4.86 (1H, d, J_{6-6a}=6.5 Hz, 6-H), and 6.37—7.60 (15H, m, ArH); MS *m/z* 516 (M$^+$).

Found: C, 74.13; H, 4.82; N, 5.32%; M^+, 516. Calcd for $C_{32}H_{24}N_2O_5$: C, 74.40; H, 4.68; N, 5.42%; M, 516.

11b: Colorless needles from ether–hexane; mp 188—190 °C; IR (KBr) 1770, 1700 (C=O), 1600, 1380, 740, and 695 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.05 (3H, s, COMe), 2.88 (1H, m, one of 7-CH_2), 3.20—3.62 (3H, m, the other of 7-CH_2, 3a-, and 7a-H), 4.48 (1H, m, 4-H), 6.40—7.32 (10H, m, ArH), and 16.02 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=24.72 (q, CO$\underline{Me}$), 27.53 (t, 7-C), 37.28, 41.57 (each d, 3a- and 7a-C), 45.62 (d, 4-C), 108.73 (s, 5-C), 126.23 (d), 128.11 (d), 128.69 (d), 128.93 (d), 129.10 (d), 131.10 (s), 137.56 (s), 175.66, 177.18 (each s, CON-), 182.00 (s, $\underline{C}$OMe), and 197.62 (s, 6-C); MS *m/z* (rel. intensity) 362 (M^++1, 26), 361 (M^+, base peak), 343 (57), 318 (47), 199 (27), 188 (48), 131 (32), 91 (29), and 77 (23).

Found: C, 72.94; H, 5.56; N, 3.87%; M^+, 361. Calcd for $C_{22}H_{19}NO_4$: C, 73.11; H, 5.30; N, 3.88%; M, 361.

A mixture of **1** (0.345 g, 1.04 mmol) and **8b** (0.519 g, 3.0 mmol) in dry benzene (6 ml) was refluxed under nitrogen for 48 h. The benzene was removed off *in vacuo*, the residue was treated with methanol (15 ml) at room temperature for 5 h, the methanol was completely evaporated *in vacuo*, and finally the viscous oil obtained was chromatographed over silica gel. The fraction with chloroform gave 0.042 g of mixtrure of **11b** (3%) and **12b** (6%), from which only **12b** was isolated by crystallization from chloroform–hexane. Continued elution with chloroform–ethyl acetate (9:1) afforded 0.43 g (80%) of **10b**.

12b: Colorless prisms from ether–hexane; mp 204—206 °C; IR (KBr) 3400 (OH), 1700 (C=O), and 1380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.13 (3H, s, COMe), 2.60 (1H, dd, J_{gem}=16.5 and J_{7-7a}=8.5 Hz, one of 7-CH_2), 2.84 (1H, dd, J_{gem}=16.5 and J_{7-7a}=2.0 Hz, the other of 7-CH_2), 3.34 (1H, ddd, J_{7a-7}=8.5, J_{7a-7}=2.0, and J_{7a-3a}=9.0 Hz, 7a-H), 3.82 (1H, dd, J_{3a-7a}=9.0 and J_{3a-4}=2.0 Hz, 3a-H), 4.77 (1H, d, J_{4-3a}=2.0 Hz, 4-H), 7.00—7.56 (10H, m, ArH), and 15.86 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=22.54 (CO$\underline{Me}$), 33.35 (7-C), 38.28, 39.99 (3a- and 7a-C), 46.26 (4-C), 107.09 (5-C), 126.28, 126.64, 127.28, 128.87, 129.22, 131.57, 139.79, 177.36 (CON-), 188.40 ($\underline{C}$OMe), and 191.87 (6-C); MS *m/z* 361 (M^+).

Found: C, 73.07; H, 5.33; N, 3.80%; M^+, 361. Calcd for $C_{22}H_{19}NO_4$: C, 73.11; H, 5.30; N, 3.88%; M, 361.

Cycloaddition of 1 to 9 Leading to I(X=O), 13, 14, and 15. A solution of **1** (0.267 g, 0.83 mmol) and **9** (0.174 g, 1.77 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 48 h. The benzene was evaporated off *in vacuo* and the residue was heated under reflux in methanol (60 ml) in the presence of *p*-toluenesulfonic acid (0.2 g) for 24 h. The methanol was removed off *in vacuo*, the residue was treated with water, extracted with ether, the ether was dried over magnesium sulfate, and finally evaporated *in vacuo* to give a viscous oil. This oil was chromatographed over silica gel using chloroform–hexane (1:2) as an eluent. The first fraction gave 0.02 g (7%) of **15** and the second 0.263 g of mixture between **13** (57%) and **14** (22%) which were separated by repeated chromatography over silica gel with ether–hexane (1:1) and crystallization.

13: Colorless needles from hexane; mp 141—143 °C; IR (KBr) 1720, 1650 (C=O), 1430, 1200, 1170, and 1000 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.25—3.85 (9H, m, CH_2 and CH), 3.10, 3.62, 3.70 (each 3H, s, COOMe), 4.13 (1H, br. d, J_{8-7}=7.5 Hz, 8-H), and 6.80—7.30 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ= 30.65 (t), 33.47 (t), 38.46, 39.51, 40.51, 42.27, 46.09, 51.02 (q), 52.13 (q), 126.35 (d), 127.34 (d), 127.93 (d), 132.62 (s), 140.61 (s), 155.58 (s), 171.90 (s), 172.67 (s), 173.25 (s), and 193.86 (s); MS *m/z* (rel. intensity) 401 (M^++1, 25), 400 (M^+, base peak), 341 (17), 340 (34), 281 (52), 249 (29), and 221 (47).

Found: C, 65.75; H, 6.08%; M^+, 400. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%; M, 400.

14: Colorless solid from hexane; mp 114—116 °C; IR (KBr) 1740, 1725, 1660 (C=O), 1440, 1200, and 1040 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.35—3.50 (9H, m, CH_2 and CH), 3.15, 3.59, 3.75 (each 3H, s, COOMe), 4.14 (1H, br. d, J_{8-7}=7.0 Hz, 8-H), and 6.90—7.30 (5H, m, ArH); MS *m/z* (rel. intensity) 401 (M^++1, 45), 400 (M^+, base peak), 369 (27), 340 (33), 309 (66), 281 (78), 277 (25), 249 (59), and 221 (91).

Found: C, 65.95; H, 6.15%; M^+, 400. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%; M, 400.

15: Colorless prisms from ether–hexane; mp 153—155 °C; IR (KBr) 1720 (C=O), 1600, and 1250—1200 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.90 (3H, s, COMe), 2.48—2.97 (2H, m, one of 6-CH_2 and 5-H), 3.06 (1H, dd, J_{gem}=20.0 and J_{6-5}=12.6 Hz, the other of 6-CH_2), 3.37 (1H, dd, J_{4-3}=2.3 and J_{4-5}= 3.2 Hz, 4-H), 3.62, 3.70 (each 3H, s, COOMe), 4.50 (1H, d, J_{3-4}=2.3 Hz, 3-H), 7.10—7.40 (5H, m, ArH), and 15.95 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=25.42 (q, CO$\underline{Me}$), 29.36 (t, 6-C), 34.64, 42.33 (each d, 4- and 5-C), 48.50 (d, 3-C), 52.08, 52.37 (each q, COO$\underline{Me}$), 106.27 (s, 2-C), 127.34 (d), 127.75 (d), 128.98 (d), 142.55 (s), 171.67, 172.61 (each s, $\underline{C}$OOMe), 179.95 (s, $\underline{C}$OMe), and 200.90 (s, 1-C); MS *m/z* (rel. intensity) 332 (M^+, 5), 301 (M^+−31, 3), 213 (21), 115 (26), 59 (20), and 43 (base peak).

Found: C, 65.19; H, 6.12%; M^+ 332. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07%; M, 332.

A solution of **1** (0.37 g, 1.11 mmol) and **9** (0.226 g, 2.3 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 48 h. The residue obtained by evaporation of the benzene *in vacuo* was triturated with benzene–hexane (1:9) to give 0.48 g (82%) of **I** (X=O) as colorless solid. The product **I** was found to contain two isomers (2.5:1) on the basis of ^{1}H-NMR spectrum (δ_{TMS}: the major isomer: 0.00 and 0.26; the minor isomer: −0.30 and 0.27). The bis-cyclo-adduct mixture **I** (X=O) (0.265 g, 0.5 mmol) was heated in water (30 ml) under reflux for 24 h. The water was evaporated to dryness *in vacuo* and the residue was washed with benzene to give 0.17 g (95%) of tricarboxylic acid. This acid (0.155 g, 0.43 mmol) was heated under reflux in methanol (100 ml) in the presence of *p*-toluenesulfonic acid (0.15 g) for 48 h. The methanol was evaporated *in vacuo*, the residue was treated with water, extracted with ether, the ether was washed with aqueous sodium hydrogencarbonate, dried over magnesium sulfate, and evaporated *in vacuo*. The residue was chromatographed over silica gel using ether–hexane (1:1) as an eluent to give 0.088 g (51%) of **13** and 0.033 g (19%) of **14**.

Similarly, **1** (0.70 g, 2.1 mmol) and **9** (0.149 g, 1.52 mmol) were stirred in dry benzene (2 ml) at room temperature under nitrogen for 72 h. The reaction mixture was added to a large quantity of hexane to precipitate colorless solid of **I** (0.25 g, 63%) which was composed of two isomers (3:1).

Cycloaddition of 2 to an Equivalent of 8a Leading to 16a. A mixture of **1** (0.662 g, 2.3 mmol) and **8a** (0.257 g, 2.3 mmol) in 1 ml of dry benzene was stirred at room temperature under nitrogen for 24 h. After evaporation of the solvent *in vacuo*, the residue was treated with methanol (15 ml) at room temperature overnight to precipitate 0.278 g of **16a**. The methanol separated from the solid was evaporated completely *in vacuo* and the viscous oil obtained was chromatographed over silica gel with hexane–ethyl acetate (3:1) to give 0.048 g of **16a**. Total amount of **16a** was 0.326 g (64%).

16a: Colorless needles from aqueous methanol; mp 186 °C; IR (KBr) 1755, 1685 (C=O), and 1640-1580 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.28 (3H, s, COMe), 2.54 (1H, dd, J_{gem}=17.0 and J_{7-7a}=15.0 Hz, one of 7-CH_2), 3.02 (1H, dd, J_{gem}=17.0 and J_{7-7a}=7.0 Hz, the other of 7-CH_2), 3.05 (3H, s, NMe), 3.60 (1H, ddd, J_{7a-7}=15.0, 7.0, and J_{7a-4}=2.5 Hz, 7a-H), 7.32 (1H, d, J_{4-7a}=2.5 Hz, 4-H), and 15.94 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=20.35 (q, CO$\underline{Me}$), 24.77 (q, NMe), 35.18 (t, 7-C), 38.12 (d, 7a-C), 108.01 (s, 5-C), 119.77 (s, 3a-C), 127.07 (d, 4-C), 167.83, 174.89 (each s, CON-), 186.07 (s, $\underline{C}$OMe), and 199.19 (s, 6-C); MS *m/z* 221 (M$^+$, base peak).

Found: C, 59.77; H, 4.93; N, 6.26%; M$^+$, 221. Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33%; M, 221.

*Cycloaddition of **2** to two Equivalents of **8a** Leading to **17a** and **18a**.* Triene **2** (0.989 g, 3.5 mmol) and **8a** (0.767 g, 7.0 mmol) were heated under reflux in dry benzene (3 ml) under nitrogen for 24 h. After cooled to room temperature, the solution was treated with 10 ml of hexane at room temperature for 0.5 h to precipitate 1.104 g (63%) of **17a**. To a solution of **17a** (0.204 g, 0.4 mmol) in 2.5 ml of dry benzene was added a drop of trifluoroacetic acid, and immediately colorless solid of **18a** was precipitated (0.125 g, 90%).

17a: Colorless solid; mp 185—187 °C; IR (KBr) 1775, 1700 (C=O), 1250, and 880 cm^{-1} (TMS); ^{1}H-NMR (CDCl$_3$) δ=0.15, 0.21 (each 9H, s, TMS), 2.26—3.65 (8H, m, CH$_2$ and CH), 2.88, 2,96 (each 3H, s, NMe), 3.09 (3H, s, OMe), and 4.70 (1H, d, J_{6-6a}=3.6 Hz, 6-H); ^{13}C-NMR (CDCl$_3$) δ=0.17, 2.17 (each q, TMS), 24.66, 24.95 (each q, NMe), 29.59, 33.35 (each t, 4- and 10-C), 36.17, 39.04, 44.50, 54.01 (each d, 3a-, 6a-, 9a-, and 10b-C), 55.72 (q, OMe), 71.10 (d, 6-C), 73.86 (s, 10a-C), 113,84 (s, 5a-C), 152.35 (s, 5-C), 175.72, 177.13, 179.01, and 180.47 (each s, CON-); MS *m/z* 508 (M$^+$), 493 (M$^+$−15), and 73 (base peak).

Found: C, 54.37; H, 7.14; N, 5.37%; M$^+$ 508. Calcd for $C_{23}H_{36}N_2O_7Si_2$: C, 54.30; H, 7.13; N, 5.51%; M, 508.

18a: Colorless prisms; mp 180—182 °C; IR (KBr) 1780 and 1720—1640 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.50—3.90 (8H, m, CH$_2$ and CH), 2.97, 3.00 (each 3H, s, NMe), 3.05 (3H, s, OMe), and 5.00 (1H, d, J_{6-6a}=4.0 Hz, 6-H); ^{13}C-NMR (CDCl$_3$) δ=24.83, 25.42 (each q, NMe), 26.42, 34.05 (each t, 4- and 10-C), 36.64, 37.57, 43.97, 45.91 (each d, 3a-, 6a-, 9a-, and 10b-C), 57.54 (q, OMe), 68.46 (d, 6-C), 135.15 (s, 5a-C), 153.00 (s, 10a-C), 173.72, 175.83, 176.71, 178.83 (each s, CON-), and 191.04 (s, 5-CO), MS *m/z* 346 (M$^+$), 331, 316 (base peak), and 314 (M$^+$−32).

Found: C, 58.94; H, 5.19; N, 8.47%; M$^+$, 346. Calcd for $C_{17}H_{18}N_2O_6$: C, 58.96; H, 5.24; N, 8.09%; M, 346.

*Cycloaddition of **2** to an Equivalent of **8b** Leading to **16b**.* A solution of **2** (0.741 g, 2.6 mmol) and **8b** (0.448 g, 2.6 mmol) in dry benzene (2 ml) was stirred at room temperature under nitrogen for 20 h and the benzene was evaporated *in vacuo*. When the residue was treated with methanol (15 ml), colorless solid of **16b** (0.536 g, 73%) was immediately separated.

16b: Colorless leaflets from dichloromethane–methanol; mp 227 °C; IR (KBr) 1765 and 1710—1610 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.25 (3H, s, COMe), 2.64 (1H, dd, J_{gem}=16.2 and J_{7-7a}=14.4 Hz, one of 7-CH$_2$), 3.07 (1H, dd, J_{gem}=16.2 and J_{7-7a}=7.1 Hz, the other of 7-CH$_2$), 3.73 (1H, ddd, J_{7a-7}=14.4, 7.1, and J_{7a-4}=2.4 Hz, 7a-H), 7.22 (1H, d, J_{4-7a}=2.4 Hz, 4-H), 7.20—7.50 (5H, m, ArH), and 16.00 (1H, s, OH); MS *m/z* 283 (M$^+$) and 136 (base peak).

Found: C, 67.83; H, 4.54; N, 5.05%; M$^+$, 283. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94%; M, 283.

*Cycloaddition of **2** to two Equivalents of **8b** Leading to **17b** and **18b**.* Triene **2** (0.515 g, 1.8 mmol) and **8b** (0.623 g, 3.6 mmol) in dry benzene (2 ml) was heated at 50 °C under nitrogen for 20 h. After cooled to room temperature, the reaction mixture was triturated with 6 ml of hexane to separate colorless precipitation of **17b** (0.704 g, 62%). To a solution of **17b** (0.19 g, 0.3 mmol) in 2.5 ml of dry benzene was added a drop of trifluoroacetic acid. The mixture was stirred at room temperature for 15 min and treated with hexane to precipitate 0.125 g (89%) of **18b**.

17b: Colorless solid; mp 188—190 °C; IR (KBr) 1775, 1705 (C=O), 1250, and 845 cm^{-1} (TMS); ^{1}H-NMR (CDCl$_3$) δ=0.19, 0.25 (each 9H, s, TMS), 2.48—3.80 (8H, m, CH$_2$ and CH), 3.20 (3H, s, OMe), 4.91 (1H, d, J_{6-6a}=3.5 Hz, 6—H), and 7.00—7.52 (10H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=1.00, 2.23 (each q, TMS), 29.77, 33.35 (each t, 4- and 10-C), 36.46, 39.16, 44.91, 54.01 (each d, 3a-, 6a-, 9a, and 10b-C), 55.95 (q, OMe), 71.74 (d, 6-C), 74.03 (s, 10a-C), 113.66 (s, 5a-C), 126.23, 126.64, 128.34, 128.98, 129.28, 131.51, 132.27, 152.76 (s, 5-C), 174.89, 176.30, 178.01, and 179.48 (each s, CON-); MS *m/z* 632 (M$^+$), 617 (M$^+$−15), and 73 (base peak).

Found: C, 62.64; H, 6.37; N, 4.65%; M$^+$, 632. Calcd for $C_{33}H_{40}N_2O_7Si_2$: C, 62.63; H, 6.37; N, 4.43%; M, 632.

18b: Colorless prisms; mp 148—150 °C; IR (KBr) 1775 and 1720—1660 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.45—3.92 (8H, m, CH$_2$ and CH), 3.12 (3H, s, OMe), 5.10 (1H, d, J_{6-6a}=4.0 Hz, 6-H), and 7.10—7.60 (10H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=26.36, 34.23 (each t, 4- and 10-C), 36.34, 37.93, 44,03, 45.85 (each d, 3a-, 6a-, 9a-, and 10b-C), 57.65 (q, OMe), 68.75 (d, 6-C), 126.05, 126.52, 128.22, 128.63, 129.10, 129.22, 131.10, 131.92, 134.97 (s, 5a-C), 152.76 (s, 10a-C), 172.67, 175.01, 175.48, 178.07 (each s, CON-), and 190.86 (s, 5-CO); MS *m/z* 438 (M$^+$−32).

Found: C, 68.45; H, 4.61; N, 6.05%. Calcd for $C_{27}H_{22}N_2O_6$: C, 68.93; H, 4.71; N, 5.95%.

*Cycloaddition of **2** to an Equivalent of **9** Leading to **19**, **20**, and **21**.* A mixture of **2** (0.904 g, 3.2 mmol) and **9** (0.309 g, 3.2 mmol) was allowed to stand at room temperature for 10 min. ^{1}H-NMR measurement of this mixture showed that **19** was formed in a quantitative yield. It was isolated as unstable liquid by vacuum distillation on a micro distillation apparatus (0.469 g, 39%). To the mixture of each equivalent of **2** and **9** was added a drop of trifluoroacetic acid, and then hexane to precipitate colorless solid of **20**.

19: Yellow liquid; bp 180 °C (133 Pa) (bulb-to-bulb); IR (neat) 1860, 1785 (C=O), 1250, and 850 cm^{-1} (TMS); ^{1}H-NMR (CDCl$_3$) δ=0.24 (18H, s, TMS), 2.48 (1H, dd, J_{gem}=16.5 and J_{7-7a}=10.0 Hz, one of 7-CH$_2$), 2.85 (1H, dd, J_{gem}=16.5 and J_{7-7a}=7.5 Hz, the other of 7-CH$_2$), 3.12 (1H, dd, J_{3a-4}=3.5 and J_{3a-7a}=10.0 Hz, 3a-H), 3.17 (3H, s, OMe), 3.47 (1H, dt, J_{7a-7}=7.5, 10.0 and J_{7a-3a}=10.0 Hz, 7a-H), 4.37, 4.63 (each 1H, d, J_{gem}=1.0 Hz, =CH$_2$), and 4.65 (1H, d, J_{4-3a}=3.5 Hz, 4-H); ^{13}C-NMR (CDCl$_3$) δ=0.59, 0.94 (each s, TMS), 28.42 (t, 7-C), 37.28, 47.26 (each d, 3a- and 7a-C), 55.83 (q, OMe), 73.27 (d, 4-C), 93.82 (t, =CH$_2$), 114.60 (s, 5-C), 151.36 (s, 6-C), 171.02, and 173.90 (each s, COO–); MS *m/z* 384 (M$^+$), 369 (M$^+$−15), and 73 (base peak).

20: Colorless needles from chloroform; mp 117—118 °C; IR (KBr) 1850, 1770 (C=O), and 1600 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=2.20 (3H, s, COMe), 2.54 (1H, dd, J_{gem}=16.5 and J_{7-7a}=9.0 Hz, one of 7-CH$_2$), 2.96 (1H, dd, J_{gem}=16.5 and J_{7-7a}=8.0 Hz, the other of 7-CH$_2$), 3.14 (3H, s, OMe), 3.26 (1H, dd, J_{3a-4}=3.0 and J_{3a-7a}=11.0 Hz, 3a-H), 3.55 (1H, m, 7a-H), 4.70 (1H, d, J_{4-3a}=3.0 Hz, 4-H), and 15.80 (1H, s, OH); ^{13}C-NMR (CDCl$_3$) δ=20.20 (q, CO$\underline{Me}$), 32.53 (t, 7-C), 35.53, 47.14 (each d, 3a- and 7a-C), 55.31 (q, OMe), 73.45 (d, 4-C), 105.27 (s, 5-C), 170.55, 173.01 (each s, COO–), 185.17 (s, $\underline{C}$OMe), and 195.91 (s, 6-C); MS *m/z* 240 (M$^+$), 209 (M$^+$−31), and 43 (base peak).

Found: C, 55.27; H, 5.03%; M$^+$, 240. Calcd for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04%; M, 240.

Crude **19**, which had been prepared from **2** (0.749 g, 2.6 mmol) and **9** (0.256 g, 2.6 mmol), was heated under reflux in methanol (50 ml) in the presence of *p*-toluenesulfonic acid (0.1 g) for 24 h. The methanol was evaporated *in vacuo* and the residue was dissolved in ether. The ether was washed with aqueous sodium hydrogencarbonate (5%), dried over magnesium sulfate, and then evaporated *in vacuo* to give viscous oil which was chromatographed over silica gel using chloroform–ethyl acetate (9:1). Colorless solid of **21** was obtained (0.371 g, 56%).

21: Colorless needles from hexane; mp 92—92.5 °C; IR

(KBr) 1725, 1690 (C=O), and 1610 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.14 (3H, s, COMe), 2.71 (1H, dd, J_{gem}=17.5 and J_{6-5}=7.0 Hz, one of 6-CH_2), 2.94 (1H, dd, J_{gem}=17.5 and J_{6-5}=3.2 Hz, the other of 6-CH_2), 3.64, 3.77 (each 3H, s, COOMe), 3.94 (1H, dd, J_{5-6}=7.0 and 3.2 Hz, 5-H), 7.54 (1H, s, 3-H), and 15.94 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=19.96, 37.22, 38.40, 51.96, 52.49, 107.13, 117.48, 134.56, 166.20, 172.37, 184.76, and 198.14; MS *m/z* 254 (M$^+$) and 195 (M$^+$−59, base peak).

Found: C, 56.59; H, 5.51%; M$^+$, 254. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55%; M, 254.

Cycloaddition of **2** *to two Equivalents of* **9** *Leading to* **K**. The reaction of **2** (0.10 g, 0.3 mmol) with **9** (0.068 g, 0.6 mmol) in benzene-d_6 (3 ml) was followed by ^{1}H-NMR spectroscopy. After 4 h at room temperature, both the starting materials were consumed and the following signals were observed: δ=0.06, 0.11 (each 9H, s, TMS), 2.10—3.50 (8H, m, CH_2 and CH), 3.00 (3H, s, OMe), and 4.75 (1H, d, J_{6-6a}=3.5 Hz, 6-H).

Cycloaddition of **1** *to* **22** *Leading to* **15**. A solution of **1** (0.53 g, 1.59 mmol) and **22** (1.44 g, 10.0 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 7 d. The usual work-up with methanol as described above and the followed column chromatography over silica gel gave 0.25 g (45%) of **15**.

Cycloaddition of **1** *to* **23a** *Leading to* **24a**, **25a**, *and* **26**. A solution of **1** (0.365 g, 1.1 mmol) and **23a** (0.476 g, 3.3 mmol) in dry benzene (5 ml) was refluxed under nitrogen for 7 d. After evaporation of all the volatile materials *in vacuo*, the residue was treated with methanol (10 ml) at room temperature overnight. The methanol was evaporated off *in vacuo* and the viscous oil obtained was chromatographed over silica gel. The fraction eluted with chloroform–hexane (1:1) afforded a mixture (0.24 g, 65%) of **24a** and **25a**. The ratio was determined by ^{1}H-NMR spectroscopy (**24a**: 55%; **25a**: 11%). They were separated into each isomer by a preparative thin-layer chromatography (silica gel) using chloroform as an eluent and purified by crystallization. The fraction with chloroform gave 0.13 g (25%) of **26**.

24a: Colorless prisms from ether-hexane; mp 83—84 °C; IR (KBr) 3400 (OH), 1725 (C=O), 1600, and 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.77 (3H, s, COMe), 2.50—3.32 (4H, m, 6-CH_2, 4-, and 5-H), 3.32, 3.65 (each 3H, s, COOMe), 4.32 (1H, m, 3-H), and 7.00—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=26.01 (s, COMe), 30.88 (t, 6-C), 39.10, 42.86 (each d, 4- and 5-C), 50.49 (d, 3-C), 51.96, 52.31 (each s, COOMe), 107.79 (s, 2-C), 127.05, 127.81, 128.09, 142.55 (s), 172.31, 173.19 (each s, COOMe), 179.30 (s, COMe), and 200.56 (s, 1-C); MS *m/z* 332 (M$^+$), 257, 195, 115, and 43 (base peak).

Found: C, 65.14; H, 6.09%; M$^+$, 332. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07%; M, 332.

25a: Colorless prisms from ether-hexane; mp 153—155 °C; IR (KBr) 3400 (OH), 1725 (C=O), 1600, and 1230 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.90 (3H, s, COMe), 2.58 (1H, dd, J_{gem}=18.5 and J_{6-5}=11.3 Hz, one of 6-CH_2), 2.70—3.40 (3H, m, the other of 6-CH_2, 4-, and 5-H), 3.53, 3.65 (each 3H, s, COOMe), 4.31 (1H, d, J_{3-4}=5.0 Hz, 3-H), and 7.10-7.35 (5H, m, ArH); MS *m/z* (rel. intensity) 332 (M$^+$, 20), 314 (21), 301 (26), 289 (62), 257 (45), 213 (26), 195 (25), and 43 (base peak).

Found: C, 64.88; H, 6.21%; M$^+$, 332. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07%; M, 332.

26: Colorless liquid as a mixture of two isomeric bisadducts (the isomer ratio was about 6—7:1). The spectral data for the major product are given as follows: ^{1}H-NMR ($CDCl_3$) δ=2.40—4.00 (8H, m, CH_2 and CH), 3.32, 3.57, 3.67, 3.83 (each 3H, s, COOMe), 4.26 (1H, br. d, J_{8-7}=5.5 Hz, 8-H), and 6.80—7.30 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ= 31.00, 37.13 (each t, 2- and 5-C), 39.67, 41.42, 42.35, 48.68 (each d, 3-, 4-, 6-, and 7-C), 49.61 (d, 8-C), 52.00, 52.53, 52.87 (each q, COOMe), 126.55, 127.53, 128.31, 134.50, 141.90, 149.40 (s, 4a-C), 170.99, 172.06, 172.70, 173.33 (each s, COOMe), and 192.48 (s, 1-CO); MS *m/z* 459 (M$^+$).

Found: C, 63.66; H, 5.78%; M$^+$, 459. Calcd for $C_{24}H_{26}O_9$: C, 63.87; H, 5.72%; M, 459.

Similar reaction of **1** (1.57 g, 4.72 mmol) with **23a** (2.16 g, 15.0 mmol) under reflux in dry toluene (10 ml) for 7 d and the same work-up as mentioned gave a mixture of **24a** (10%) and **25a** (2%), and **26** (88%).

Cycloaddition of **1** *to* **23b** *Leading to* **24b** *and* **25b**. Triene **1** (0.75 g, 2.25 mmol) and **23b** (0.527 g, 6.75 mmol) in toluene (6 ml) were allowed to react under the conditions shown in Table 3. The usual work-up with methanol and the followed chromatography over silica gel with chloroform afforded a mixture (0.386 g, 64%) of **24b** and **25b**. The isomer ratio was found be 2:11 (**24b**: 10%; **25b**: 55%). Only the major product **25b** was isolated as colorless solid which solidified when the above mixture was treated with methanol.

25b: Colorless needles from methanol; mp 210—211.5 °C; IR (KBr) 3400 (OH), 2250 (CN), and 1590 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.76 (3H, s, COMe), 2.80—3.00 (4H, m, 6-CH_2, 4-, and 5-H), 4.33 (1H, d, J_{3-4}=8.5 Hz, 3-H), and 7.10—7.44 (5H, m, ArH); MS *m/z* (rel. intensity) 267 (M$^+$+1, 12), 266 (M$^+$, 40), 248 (61), 221 (26), 195 (21), 170 (28), 168 (36), 167 (26), 155 (27), 145 (28), 117 (27), 81 (24), and 43 (base peak).

Found: 71.88; H, 5.20; N, 10.28%; M$^+$, 266. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52%, M, 266.

Cycloaddition of **2** *to* **22** *Leading to* **M** *and* **21**. A mixture of **2** (0.779 g, 2.7 mmol) and **22** (0.392 g, 2.7 mmol) in dry benzene (3 ml) was heated under reflux under nitrogen for 48 h. The benzene was evaporated *in vacuo*, the residue was treated with methanol (15 ml) at room temperature overnight, and the methanol was removed off *in vacuo*. Viscous oil obtained was chromatographed over silica gel using chloroform-ethyl acetate (9:1) to give 0.293 g (42%) of **21** which was identical with a product given in the reaction of **2** with maleic anhydride **9**.

Similar reaction of **2** with three equivalents of **22** was carried out under reflux in dry benzene for 72 h. After all the volatile materials were removed off *in vacuo*, the residue was submitted for ^{1}H-NMR measurement. The spectrum showed the quantitative formation of exo mono-cycloadduct M: ^{1}H-NMR ($CDCl_3$) δ=0.18, 0.23 (each 9H, s, TMS), 2.20—3.50 (4H, m, 6-CH_2, 4-, and 5-H), 3.37 (3H, s, OMe), 3.60, 3.69 (each 3H, s, COOMe), 4.40, 4.60 (each 1H, s, =CH_2), and 4.48 (1H, d, J_{3-4}=2.8 Hz, 3-H).

Cycloaddition of **2** *to* **23a** *Leading to* **21**. Similar reaction starting from **2** (0.461 g, 1.6 mmol) and **23a** (0.234 g, 1.6 mmol) under the conditions shown in Table 3 and the same work-up as mentioned above gave 0.336 g (82%) of **21**.

Cycloaddition of **1** *to* **27a** *Leading to* **28a** *and* **29a**. Triene **1** (0.92 g, 2.72 mmol) and **27a** (5 ml, large excess) in dry benzene (3 ml) were refluxed under nitrogen for 6 d. After all the volatile materials were evaporated *in vacuo*, the residue was treated with methanol (20 ml) at room temperature overnight. The methanol was removed off *in vacuo* and the residue was chromatographed over silica gel using chloroform-hexane (1:1) to give 0.34 g (48%) of **28a** and then 0.14 g (20%) of **29a**.

28a: Colorless prisms from hexane; mp 31—32 °C; IR (KBr) 3400 (OH), 1700 (C=O), and 1598 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.75—2.00 (2H, m, 5-CH_2), 1.85, 2.15 (each 3H, s. COMe), 2.42 (2H, m, 6-CH_2), 2.74 (1H, dt, J_{4-5}=5.2 and J_{4-3}=4.0 Hz, 4-H), 4.31 (1H, d, J_{3-4}=4.0 Hz, 3-H), and 7.00—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=19.55 (t, 5-C), 25.71 (q, COMe), 28.24 (t, 6-C), 28.36 (q, COMe), 40.92 (d, 4-C), 55.31 (d, 3-C), 108.14 (s, 2-C), 126.70, 127.69, 128,69, 144.48, 180.47 (s, 2-COMe), 200.90 (s, 4-COMe), and 208.47 (1-CO); MS *m/z* (rel. intensity) 258 (M$^+$, 16), 215 (49), 197 (33), 173 (21), 155 (31), and 43 (base peak).

Found: C, 74.62; H, 6.97%; M$^+$, 258. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%; M, 258.

29a: Colorless grains from hexane; mp 81—82 °C; IR (KBr) 3400 (OH), 1700 (C=O), and 1590 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.80—2.30 (2H, m, 5-CH_2), 1.85, 1.88 (each 3H, s, COMe), 2.55 (2H, m, 6-CH_2), 2.83 (1H, ddd, J_{4-5}=4.0, 12.1, and J_{4-3}=4.9 Hz, 4-H), 4.26 (1H, d, J_{3-4}=4.9 Hz, 3-H), 6.90—7.36 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=17.79 (t, 5-C), 25.36, 28.83 (each q, CO$\underline{\text{Me}}$), 29.82 (t, 6-C), 42.74 (d, 4-C), 52.66 (d, 3-C), 109.73 (s, 2-C), 127.34 (d), 128.46 (d), 128.93 (d), 139.73 (s), 180.59 (s, 2-$\underline{\text{C}}$OMe), 200.79 (s, 4-$\underline{\text{C}}$OMe), and 209.65 (s, 1-CO); MS *m/z* (rel. intensity) 259 (M$^+$+1, 48),258 (M$^+$, base peak), 215 (63), 197 (41), 187 (23), 173 (23), 155 (27), 131 (22), and 43 (61).

Found: C, 74.39; H, 7.01%; M$^+$, 258. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%; M, 258.

*Cycloaddition of **1** to **27b** Leading to **28b** and **29b**.* Similar reaction of **1** (0.376 g, 1.13 mmol) with **27b** (2 ml) in benzene (6 ml) followed by the work-up with methanol afforded the crude product which was then chromatographed over silica gel. The fraction eluted with chloroform–hexane *(3:7) gave 0.11 g of* **28b** *and the continued fraction 0.15 g of* mixture between **28b** and **29b** (**28b**: 35%; **29b**: 13%). The fraction with chloroform–hexane (1:1) provided 0.028 g of **29b**. Total amount of **28b** was 0.22 g (70%) and that of **29b** was 0.068 g (22%).

28b: Pale yellow liquid by repeated column chromatography; IR (neat) 3400 (OH), 1720 (C=O), and 1595 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.60—2.10 (2H, m, 5-CH_2), 1.88 (3H, s, COMe), 2.30—2.60 (2H, m, 6-CH_2), 2.76 (1H, dt, J_{4-5}= 4.5 and J_{4-3}=3.4 Hz, 4-H), 3.71 (3H, s, COOMe), 4.40 (1H, d, J_{3-4}=3.4 Hz, 3-H), and 7.00—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=18.85 (t, 5-C), 25.60 (q, CO$\underline{\text{Me}}$), 27.95 (t, 6-C), 41.92 (d, 4-C), 47.03 (d, 3-C), 52.08 (q, COO$\underline{\text{Me}}$), 107.68 (s, s, 2-C), 126.87 (d), 127.81 (d), 128.75 (d), 143.96 (s), 173.66 (s, $\underline{\text{C}}$OOMe), 180.94 (s, $\underline{\text{C}}$OMe), and 201.08 (s, 1-CO); MS *m/z* 274 (M$^+$), 231, and 196.

Found: C, 70.19; H, 6.67%; M$^+$, 274. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%; M, 274.

29b: Colorless prisms from ether-hexane; mp 93—95 °C; IR (KBr) 3400 (OH), 1730 (C=O), 1600, 1400, and 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.70—3.04 (5H, m, 5-, 6-CH_2, and 4-H), 1.89 (3H, s, COMe), 3.56 (3H, s, COOMe), 4.29 (1H, d, J_{3-4}=5.0 Hz, 3-H), and 6.90-7.35 (5H, m, ArH); MS *m/z* (rel. intensity) 275 (M$^+$+1, 18), 274 (M$^+$, base peak), 231 (58), 197 (37), 155 (20), 145 (21), and 42 (53).

Found: C, 69.93; H, 6.87%; M$^+$ 274. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%; M, 274.

*Cycloaddition of **1** to **27c** Leading to **28c** and **29c**.* Triene **1** (0.65 g, 1.95 mmol) was heated under reflux in freshly distilled **27c** (5 ml) under nitrogen for 58 h. The crude product obtained by the usual work-up with methanol was chromatographed over silica gel. The fraction eluted with chloroform–hexane (2:1) afforded 0.084 g of **28c**, and then 0.21 g of **28c** and **29c** (3.3:1). The other fraction with chloroform gave 0.045 g of **29c**. Total amount of **28c** was 0.245 g (54%) and that of **29c** was 0.094 g (18%).

28: Colorless prisms from ether-hexane; mp 153—155 °C; IR (KBr) 3400 (OH), 2230 (CN), 1590, 1410, 1240, and 960 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.60-2.10 (2H, m, 5-CH_2), 1.88 (3H, s, COMe), 2.48 (1H, dt, J_{gem}=19.0 and J_{6-5}=4.5 Hz, one of 6-CH_2), 2.86 (1H, dt, J_{gem}=19.0 and J_{6-5}=9.0 Hz, the other of 6-CH_2), 3.00 (1H, dt, J_{4-5}=4.1 and J_{4-3}=2.7 Hz, 4-H), 4.20 (1H, d, J_{3-4}=2.7 Hz, 3-H), and 7.00—7.44 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=18.85 (t, 5-C), 25.42 (t, 6-C), 27.30 (q, CO$\underline{\text{Me}}$), 33.17 (d, 4-C), 43.44 (d, 3-C), 105.97 (s, 2-C), 120.59 (s, CN), 127.89, 129.10, 141.25, 180.18 (s, $\underline{\text{C}}$OMe), and 201.03 (s, 1-CO); MS *m/z* (rel. intensity) 241 (M$^+$, 28), 214 (26), 196 (23), 187 (22), 155 (37), 145 (35), 115 (29), 77 (26), and 44 (base peak).

Found: C, 74.88; H, 6.34; N, 5.84%; M$^+$, 241. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81%; M, 241.

29c: Colorless prisms from ether-hexane; mp 144—146 °C; IR (KBr) 3400 (OH), 2220 (CN), 1600, 1410, 1240, and 940 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.86 (3H, s, COMe), 1.94 (2H, m, 5-CH_2), 2.59 (2H, dd, J_{6-5}=6.1 and 7.1 Hz, 6-CH_2), 3.10 (1H, m, 4-H), 4.09 (1H, d, J_{3-4}=4.9 Hz, 3-H), and 7.10—7.50 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=18.85 (t, 5-C), 25.48 (t, 6-C), 29.30 (q, CO$\underline{\text{Me}}$), 32.25 (d, 4-C), 41.63 (d, 3-C), 108.03 (s, 2-C), 119.77 (s, CN), 128.16, 128.63, 129.34, 138.09, 179.18 (s, $\underline{\text{C}}$OMe), and 200.85 (s, 1-CO); MS *m/z* (rel. intensity) 241 (M$^+$, 35), 214 (22), 187 (21), 155 (33), 145 (32), and 77 (23).

Found: C, 74.68; H, 6.31; N, 5.83%; M$^+$, 241. Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81%; M, 241.

Similar reaction of **1** (0.769 g, 2.3 mmol) with **27c** (3.1 ml, 46 mmol) was carried out in a sealed tube (At 110 °C for 5 d in 6 ml of dry benzene). The usual work-up with methanol gave viscous oil which was purified by chromatography over silica gel. The fraction eluted with hexane–ethyl acetate *(4:1) afforded 0.116 g of* **28c** *and 0.065 g of mixture between* **28c** and **29c** (1:1). The continued elution with hexane–ethyl acetate (2:1) gave 0.243 g of **30**. Total amounts were as follows: **28c**: 0.149 g (27%); **29c**: 0.033 g (6%); **30**: 0.243 g (38%). The bis-adduct **30** was found to be a mixture of two isomers whose ^{1}H-NMR spectrum was given as shown below: ^{1}H-NMR ($CDCl_3$) δ=1.68—2.10 (2H, m, CH_2), 2.10—3.10 (7H, m, CH_2 and CH), 3.44—3.80 (1H, m, C$\underline{\text{H}}$CN), 4.37 (1H, br. C$\underline{\text{H}}$Ph), and 6.80—7.44 (5H, m, ArH).

*Cycloaddition of **2** to **27a** Leading to **31a**.* A solution of **2** (0.856 g, 3.0 mmol) and freshly distilled **27a** (1.2 ml, 15 mmol) was heated under reflux in dry benzene (3 ml) under nitrogen for 48 h. The usual work-up with methanol gave the crude product. It was chromatographed over silica gel using hexane–chloroform (3:1) to give 0.325 g (60%) of **31a**.

31a: Colorless prisms from ether-hexane; mp 42—44 °C; IR (KBr) 1680—1540 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.28, 2.36 (each 3H, s, COMe), 2.50—2.70 (4H, m, CH_2), 7.32 (1H, br. s, 3-H), and 16.23 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=20.14 (t, CH_2), 20.31, 24.95 (each q, CO$\underline{\text{Me}}$), 34.05 (t, CH_2), 107.56 (s), 129.81 (s), 133.27 (d, 3-C), 185.40 (s, 2-$\underline{\text{C}}$OMe), 196.50 (s, 4-$\underline{\text{C}}$OMe), and 199.91 (s, 1-C); MS *m/z* 180 (M$^+$), 137 (M$^+$−43), and 43 (base peak).

Found: C, 66.91; H, 6.79%; M$^+$, 180. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%; ,M, 180.

*Cycloaddition of **2** to **27b** Leading to **31b**.* Similar procedure starting from **2** (0.81 g, 2.8 mmol) and **27b** (0.73 g, 8.4 mmol) and the followed column chromatography over silica gel using chloroform gave 0.367 g (66%) of **31b**. The reaction conditions were listed in Table 3.

31b: Colorless needles from aqueous methanol; mp 60 °C; IR (KBr) 1700 and 1640—1580 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.23 (3H, s, COMe), 2.40—2.80 (4H, m, CH_2), 3.75 (3H, s, COOMe), 7.40 (1H, br. s, 3-H), and 16.07 (1H, s, OH); ^{13}C-NMR ($CDCl_3$) δ=20.20 (q, CO$\underline{\text{Me}}$), 21.37, 34.35 (each t, CH_2), 51.72 (q, COO$\underline{\text{Me}}$), 107.73 (s), 120.00 (s), 132.74 (d, 3-C), 167.14 (s, $\underline{\text{C}}$OOMe), 184.64 (s, $\underline{\text{C}}$OMe), and 199.79 (s, 1-CO); MS *m/z* 196 (M$^+$), 181 (M$^+$−15), and 43 (base peak).

Found: C, 61.07; H, 6.23%; M$^+$, 196. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16%; M, 196.

*Cycloaddition of **2** to **27c** Leading to **31c**.* The same procedure using **2** (0.765 g, 2.7 mmol) and **27c** (0.88 ml, 13.5 mmol) and the followed column chromatography over silica gel using dichloromethane gave 0.316 g (73%) of **31c**. The reaction conditions were shown in Table 3.

31c: Colorless prisms from dichloromethane-hexane; mp 108—109 °C; IR (KBr) 2200 (CN) and 1680—1500 cm^{-1}

(C=O); ^{1}H-NMR (CDCl$_3$) δ=2.20 (3H, s, COMe), 2.60 (4H, m, CH$_2$), 7.04 (1H, s, 3-H), and 16.03 (1H, s, OH); ^{13}C-NMR (CDCl$_3$) δ=20.14 (q, CO$\underline{\text{Me}}$), 23.78, 33.58 (each t, $\underline{\text{C}}$H$_2$), 107.73 (s, 2-C), 111.96 (s), 119. 65 (s, CN), 137.67 (d, 3-C), 184.70 (s, $\underline{\text{C}}$OMe), and 198.03 (s, 1-CO); MS m/z 163 (M$^+$, bask peak).

Found: C, 66.38; H, 5.65; N, 8.43%; M$^+$, 163. Calcd for C$_9$H$_9$NO$_2$: C, 66.25; H, 5.56; N, 8.58%; M, 163.

The present work was partially supported by a Grant-in-Aid for Scientific Research No.58750694 from the Ministry of Education, Science and Culture to E. W.

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13) Both **1** and **2** can be purified by a chromatography over silica gel (Wako gel C200) using hexane–benzene mixture (9:1), but with poor recovery (30—50%).

14) The trienes can be stored in a freezer under nitrogen in the presence of hydroquinone. The polymerization inhibitor is needed only for **1**. No detectable decomposition has been observed at least in one month under the above conditions. Prior to their use, they are purified by a vacuum distillation on a bulb-to-bulb distillation apparatus.

15) It is known that a trans diene undergoes the Diels-Alder reaction much faster than a cis diene (J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967) and references cited therein).

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