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Studies on Synthesis of 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene Derivatives. II.[1] Synthesis and Structural Confirmation of Photocycloadducts, 8,9-Dimethoxycarbonyl-2:3,5:6-dibenzobicyclo[5.2.0]nonan-4-one and Related Compounds, Using Two-Dimensional Nuclear Magnetic Resonance Spectrometry

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The photochemical reaction of dibenzo[*a*,*d*]cyclohepten-5-one (**1**) with dimethyl maleate or dimethyl fumarate in dioxane under external irradiation with a 100 W high pressure Hg lamp readily afforded a cycloadduct **2a** in high yield along with the stereoisomer **3a**. The adducts **2a** and **3a** were individually subjected to hydrolysis, followed by esterification with diazomethane, to afford four isomeric compounds **4a**, **5a**, **6a**, and **7a**. The stereostructures of **6a** and **7a**, stereoisomers of a dibenzotricyclo compound, were elucidated on the basis of intramolecular hydrogen bonding studies, and the chemical structures of the six compounds (**2a**, **3a**, **4a**, **5a**, **6a**, and **7a**) were investigated.

Two-dimensional INADEQUATE, $^{13}C/^{1}H$ shift correlation, and ^{1}H–^{1}H nuclear Overhauser effect (NOE) experiments were performed in order to verify the stereostructure of **2a** including the conformation. Total ^{13}C and ^{1}H assignments of **2a** have been obtained unambiguously and the stereostructure was also determined from the NOE data.

Keywords——dibenzo[*a*,*d*]cyclobutanocycloheptene derivative; 2:3,5:6-dibenzotricyclo-[5.2.0.0^{4,8}]nonane derivative; [2+2]photocycloaddition; stereochemistry; transannular cyclization; two-dimensional NMR; ^{1}H–^{1}H NOE; ^{13}C–{^{1}H} NOE

Previously, the authors reported a synthesis of *N*-alkyl-10-hydroxy-10,5-(iminometha-no)-5*H*,10*H*-dibenzo[*a*,*d*]cyclohepten-11-ones,[2] which showed potent analgesic activity. The stereostructures of these compounds are of great interest.

The present paper deals with a synthesis of 2:3,5:6-dibenzobicyclo[5.2.0]nonane derivatives through photocycloaddition of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**1**) with dimethyl maleate or fumarate and describes the chemical properties of photocycloadducts, as well as the stereochemistry[3] of one of the adducts **2a** as determined by using one- and two-dimensional nuclear magnetic resonance (NMR) techniques.[4]

Synthesis and Chemical Structure

A photocycloaddition reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**1**) with dimethyl maleate or fumarate in dioxane was undertaken by the external irradiation method using a high-pressure Hg lamp in a quartz or Pyrex vessel for 20—30 h under a nitrogen atmosphere, and afforded an adduct (**2a**), mp 156 °C, in 75—80% yield and another isomer (**3a**), mp 134—136 °C, in 7—8% yield (Chart 1).

Isomerization reaction of **2a** with sodium hydride in dimethylformamide (DMF) at 60 °C proceeded to afford an alcohol (**6a**), mp 212 °C, as a major product and a small amount of a diester (**4a**), mp 179 °C. When the same reaction was carried out at 80 °C, **4a**, **6a**, and an

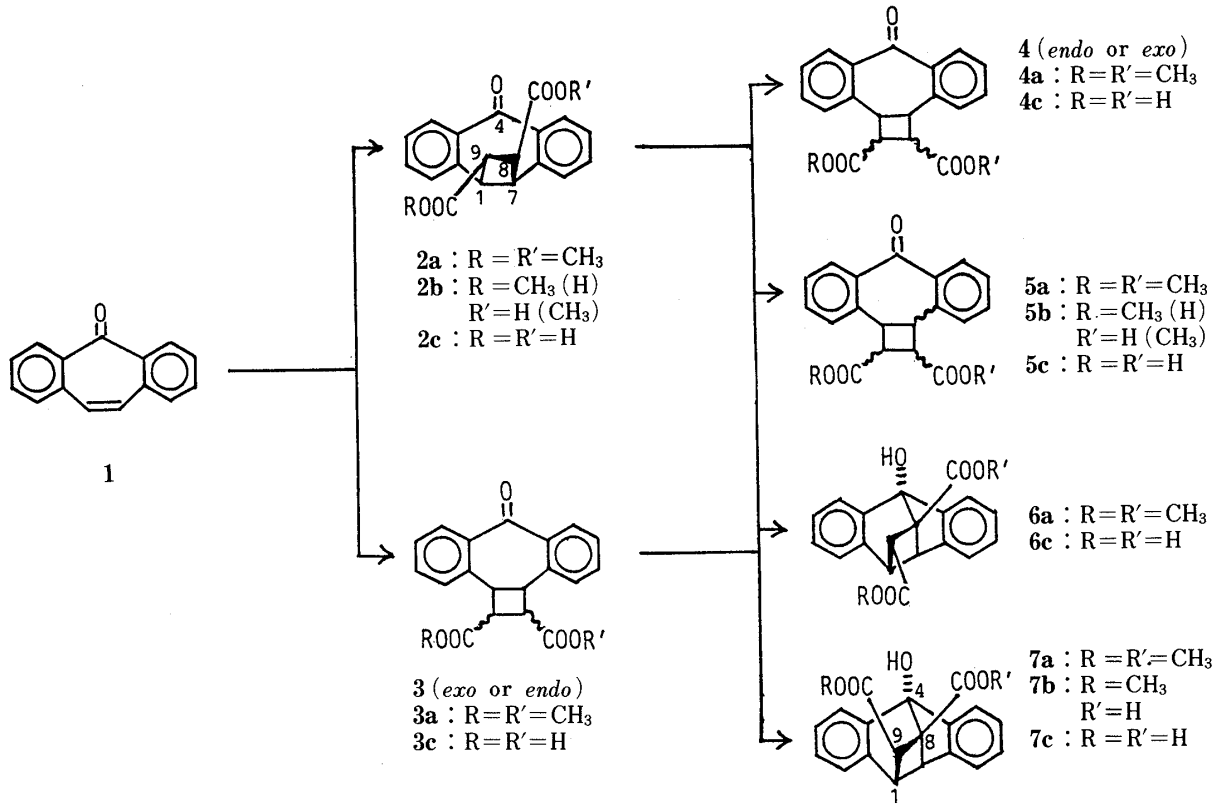


Chart 1

alcohol (**7a**), mp 157 °C, were obtained in 50—60%, 8—15%, and 15—29% yields, respectively.

The same reaction of **3a** gave the same products **4a**, **6a**, and **7a** in almost the same ratio as above. When the adduct (**2a**) was heated under reflux with a solution of potassium hydroxide–ethanol–water for 5 h and the resulting carboxylic acids were esterified with diazomethane, **4a**, **6a**, and a new diester (**5a**), mp 193 °C, were formed in 40%, 16%, and 4% yields, respectively. The same reactions of **3a** also led to almost the same result. Consequently, four products (**4a**, **5a**, **6a**, and **7a**) were obtained in the above-mentioned reactions of **2a** and **3a**.

These experiments strongly suggested that these compounds were stereoisomers at carbon atoms carrying methoxycarbonyl groups and/or at benzyl positions. Structural assignment of the products (**4a**, **5a**, **6a**, and **7a**) and starting materials (**2a** and **3a**) was attempted with spectrometrical tools such as infrared absorption (IR), ^{1}H- and ^{13}C-NMR and mass spectra (MS), and the results are listed in Table I.

In **2a**, **3a**, **4a**, **5a**, **6a**, and **7a**, elementary analysis data all agreed with the theoretical value for $C_{21}H_{18}O_5$ and the MS of each showed $M^+ = 350$ *m/z*. From the spectral data (Table I), these compounds (**2a**, **3a**, **4a**, and **5a**) were concluded to be four stereoisomers of 8,9-dimethoxycarbonyl-2 : 3,5 : 6-dibenzobicyclo[5.2.0]nonan-4-one having different configurations and/or conformations.

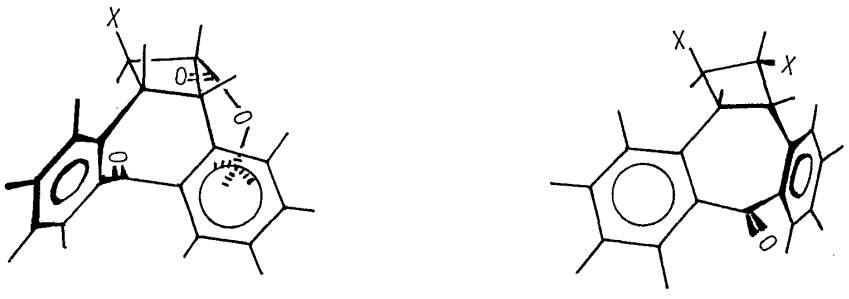
Moreover, based upon stereomodels of the cyclobutano-dibenzocycloheptene, two preferred conformations, as in the case of the *cis* ring juncture, are presented in Fig. 1. Many examples of such conformational analysis have been reported.[5)]

In the present case, it might be considered that the ring juncture of **3a** and **4a** between the four- and seven-membered ring is *cis* and the conformation of the **3a** ring system is similar to that in the **4a** ring system because both **3a** and **4a** have a molecular symmetry which is clear from the ^{1}H- and ^{13}C-NMR spectra. However, it could not be clarified which one of **3a** and **4a** is the *endo*- or *exo*-adduct from above-mentioned spectral data. Abnormal chemical shift of

TABLE I. 8,9-Dimethoxycarbonyl-2:3,5:6-dibenzobicyclo[5.2.0]nonan-4-ones (**2a**, **3a**, **4a**, and **5a**) and 8,9-Dimethoxycarbonyl-4-hydroxy-2:3,5:6-dibenzotricyclo[5.2.0.0^{4,8}]nonanes (**6a** and **7a**)

Compd. No.	mp (°C)	IR (KBr) cm^{-1}			^{1}H-NMR ($CDCl_3$) δ				^{13}C-NMR[a]						MS (m/z)
		COO	CO	OH	Cyclobutane ring H	CH_3	Ar–H	OH	Cyclobutane ring C	CH_3	COO	C=O	C–OH		
2a	156	1730 1740	1660		3.65—4.60 (4H) m	3.22 (3H) s 3.61 (3H) s	6.95—7.85 (8H) m		43.5 46.9	45.5 47.3	51.6 51.8	169.3 172.6	199.4		350 (M^+) 318 290 231 206[b] 193 178
3a	136	1725 1730	1665		3.44 (2H) m 4.47 (2H) m	3.70 (6H) s	7.15—7.70 (8H) m		44.4	47.9	52.2	172.0	200.4		350 (M^+) 318 291 231 206[b] 193 178
4a	179	1730 1740	1635		3.81 (4H) s	3.81 (6H) s	7.30—7.60 (6H) m 8.19 (2H) dd		43.5	45.8	52.4	172.1	191.8		350 (M^+) 318 290 231[b] 193
5a	193	1730 1740	1635		3.65—4.05 (3H) m 4.77 (1H) t-like	3.64 (3H) s 3.74 (3H) s	7.07 (1H) dd 7.20—7.60 (4H) m 7.91 (1H) dd 8.28 (1H) dd		42.2 45.3	44.3 46.4	51.9 52.1	171.6 172.0	193.4		350 (M^+) 318 290 231[b] 193
6a	212	1710 1740		3420	2.80 (1H) s 3.82 (1H) d 4.89 (1H) d	3.65 (3H) s 3.78 (3H) s	6.75—7.35 (7H) m 7.55 (1H) dd	4.42 (1H) br s	44.3 52.6	50.9 65.7	51.4 52.0	170.8 173.3		87.3	350 (M^+) 300 290 231[b] 193
7a	157	1720 1740		3460	3.85—4.15 (3H) m	3.27 (3H) s 3.67 (3H) s	6.75—7.60 (8H) m	4.20 (1H) s	44.2 52.4	45.7 65.2	51.4 52.0	171.0 171.4		84.9	350 (M^+) 300 290 231[b] 215

a) ppm from TMS as an internal reference in $CDCl_3$ except **6a** (measured in $CDCl_3$–DMSO-d_6). *b*) Base peak. ^{1}H- and ^{13}C-NMR were measured at 80 MHz (^{1}H) and at 20 MHz (^{13}C).



A-form B-form

X=$COOCH_3$

Fig. 1. Possible Conformations of 8,9-Dimethoxycarbonyl-2:3,5:6-dibenzobicyclo[5.2.0]nonan-4-one (**2a**) Based on Stereomodel

the proton signal at δ 3.22 (CH_3) of **2a** due to anisotropy of the benzene ring[6] (described later) and close similarity of the **2a** fragment pattern to that of **3a**, and of the **4a** fragment pattern to that of **5a** in the MS were observed.

In the case of **6a** and **7a**, the IR spectra showed an OH absorption at 3420 and 3460 cm^{-1}, respectively, and in the ^{1}H-NMR, one proton signal of the cyclobutane ring had disappeared and a proton signal (D-exchangeable) appeared at δ 4.42 and 4.20, respectively. In the ^{13}C-NMR, a carbonyl carbon signal appeared at δ 199.4 in **2a** and at δ 200.4 in **3a**, but in **6a** and **7a** the carbonyl signals located near δ 200 had disappeared and a new quaternary carbon signal was found at δ 87.3 in **6a** and at δ 84.9 in **7a**. Furthermore, another quaternary carbon, which would correspond to a carbon atom on cyclobutane ring, appeared at δ 65.7 in **6a** and at δ 65.2 in **7a**. MS fragment patterns of **6a** and **7a** were almost the same. Taking these spectral data into consideration, **6a** and **7a** were concluded to be stereoisomers of 8,9-dimethoxycarbonyl-4-hydroxy-2:3,5:6-dibenzotricyclo[5.2.0.$0^{4,8}$]nonane (no methine proton signal at C-8 was observed), formed by transannular bridging between C-4 and C-8.

In order to clarify the configuration of the methoxycarbonyl group at C-9 in **6a** and **7a** the existence of intramolecular hydrogen bonding was investigated. The IR spectra of **6a** and **7a** were measured by a high dilution method in chloroform solution (concentration: 0.15 and 0.005 mol/l), and an intramolecular hydrogen bonding was found in the case of **7a** (it was considered that the hydrogen bonding existed between the hydroxyl group at C-4 and the methoxycarbonyl group at C-9), but not **6a**. Thus, the relative configuration of the methoxycarbonyl group at the 9-position in **6a** and **7a** was clarified as depicted in Chart 1.

Hydrolysis with some bases and sodium borohydride reduction on **2a**—**7a** were carried out (Charts 1 and 2). Thus, heating of **2a** with sodium carbonate–methanol–water afforded **2b** as colorless needles, mp 224 °C, in an excellent yield. The elementary analysis data agreed with the theoretical values for $C_{20}H_{16}O_5$. In the ^{1}H-NMR, a methyl group signal located at δ 3.61 in **2a** disappeared and a new broad signal appeared near δ 6.3 (COOH), so the product was considered to be a monocarboxylic acid (**2b**) formed by selective hydrolysis of methoxycarbonyl groups. Compound **2b** was treated with diazomethane or ① $SOCl_2$– ② CH_3OH to reform **2a** quantitatively. The acid chloride of the monocarboxylic acid (**2b**) was treated with methanol-d_4 to afford the corresponding diester (**2a**-d_3). From a comparison of the ^{1}H-NMR spectra of **2a** with **2a**-d_3, it was clarified that a methyl group at δ 3.61 was more easily hydrolyzable than the other in **2a**; in other words, the former methyl group was less hindered than the latter as regards the attack of water. Similar hydrolysis was carried out for **3a**—**7a**; **7b** was obtained quantitatively from **7a** and **5b** was obtained in good yield from **5a**. Each of **3a** and **4a** was also hydrolyzed to give the corresponding dicarboxylic acid (**3c** and **4c**). Interestingly, it was found that **2b** was obtained in 43% yield from **6a** by hydrolysis.

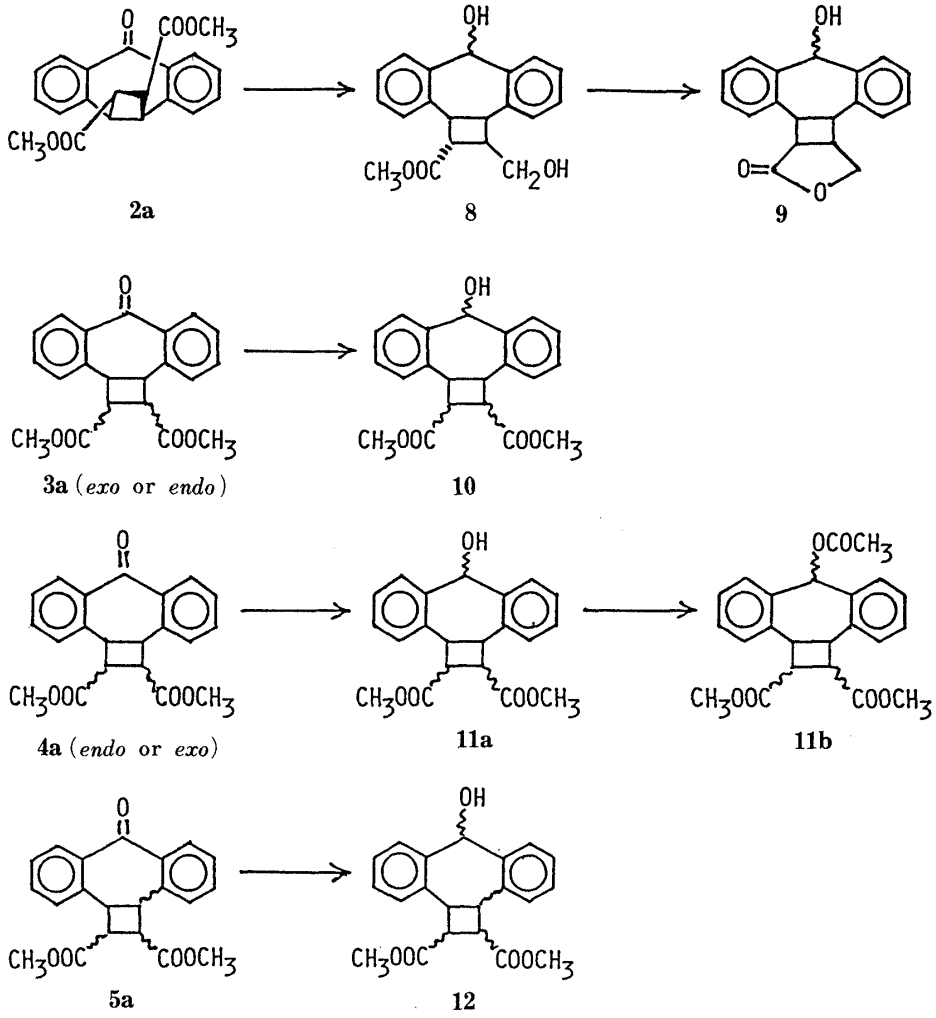


Chart 2

The diesters **2a**—**7a** were kept standing for several hours or heated for a short time in KOH–ethanol to afford the corresponding dicarboxylic acids (**2c**—**7c**) quantitatively, all of which reformed the original diesters on treatment with diazomethane. The diester **2a** was not reduced with $NaBH_4$ (4 mol eq in methanol–water), but it was reduced with excess $NaBH_4$ to form a diol ester (**8**), mp 174 °C, in 76% yield. The elementary analysis data coincided with the theoretical values for $C_{20}H_{20}O_4$. The IR spectrum showed the presence of hydroxyl group (3375 cm^{-1}) and carbonyl group (1700 cm^{-1}) absorptions. The ^{1}H-NMR spectrum revealed a D-exchangeable signal (2H), a broad signal (2H) and a less broad singlet signal (1H) at δ 1.7, 3.9, and 5.98, respectively. In the ^{13}C-NMR, signals at δ 67.7 (>$\underline{C}$HOH) and 63.3 (–$\underline{C}H_2$OH) were detected. Therefore, the compound, mp 174 °C, was identified as a new diol ester (**8**) formed by simultaneous reduction of the C-4 carbonyl group and the methoxycarbonyl group. Treating **8** with a base gave colorless prisms, mp 274 °C; the elementary analysis data were consistent with the theoretical values for $C_{19}H_{16}O_3$. The IR spectrum showed the presence of hydroxyl group (3450 cm^{-1}) and esteric carbonyl group (1745 cm^{-1}) absorptions and no methyl signal ($COOC\underline{H}_3$) was detected in the ^{1}H-NMR. Thus, the compound was assigned as a lactone (**9**), which was confirmed to be a five-membered one on the basis of the finding that a ^{13}C-NMR signal (–$\underline{C}H_2$–) of **8** at δ 63.3 shifted markedly to lower field at δ 73.2. Suspensions of powdered **3a** and **4a** in methanol–water were each treated with $NaBH_4$ to form **10**, mp 166.5 °C, and amorphous **11a**, which was esterified with acetic anhydride–pyridine to give **11b**, mp 148—150 °C. The structures of the compounds (**10** and **11b**) were identified by

elementary analysis, and IR and ^{1}H-NMR spectrometry. Similar $NaBH_4$ reduction of **5a** also proceeded easily to form **12**, mp 143—150 °C, which gave analytical values in agreement with $C_{21}H_{20}O_5$ but was shown to be a mixture of epimeric alcohols by thin layer chromatography and ^{1}H-NMR spectroscopy. The product was so unstable that each alcohol could not be obtained in a pure state.

Determination of Relative Configuration and Conformation of 2a by Two-Dimensional (2D) NMR and Nuclear Overhauser Effect (NOE)

In order to obtain unambiguous total ^{13}C and ^{1}H assignments of **2a** 2D carbon double quantum coherence[7] (2D INADEQUATE) and ^{13}C/^{1}H chemical shift correlation[8] (CH-COSY) experiments were carried out. Observed spectra are shown in Figs. 2 and 3.

In the 2D INADEQUATE spectra (Fig. 2), each directly bonded ^{13}C–^{13}C pair appears as a pair of AX or AM doublets which have the same double quantum frequency, *i.e.*, falling on the same horizontal line. Each doublet is centered about the corresponding chemical shift in the standard ^{1}H-decoupled ^{13}C spectrum with the doublet splitting, $^1J_{C-C}$. Furthermore, each AX or each AM spectrum must be symmetric about a line of slope 2 which passes through the origin defined by the radio-frequency carrier (the diagonal lines in Fig. 2).[7a] These severe constraints allow us to establish the carbon–carbon connectivity easily by inspection of the spectral patterns.

Thus, most of the ^{13}C assignments were straightforwardly determined, that is, starting from the readily identifiable C(4) resonance ($\delta = 199.48$) carbon–carbon bond networks for a seven-membered ring, C(4)–C(3)–C(2)–C(1)–C(7)–C(6)–C(5)–C(4), for a four-membered ring,

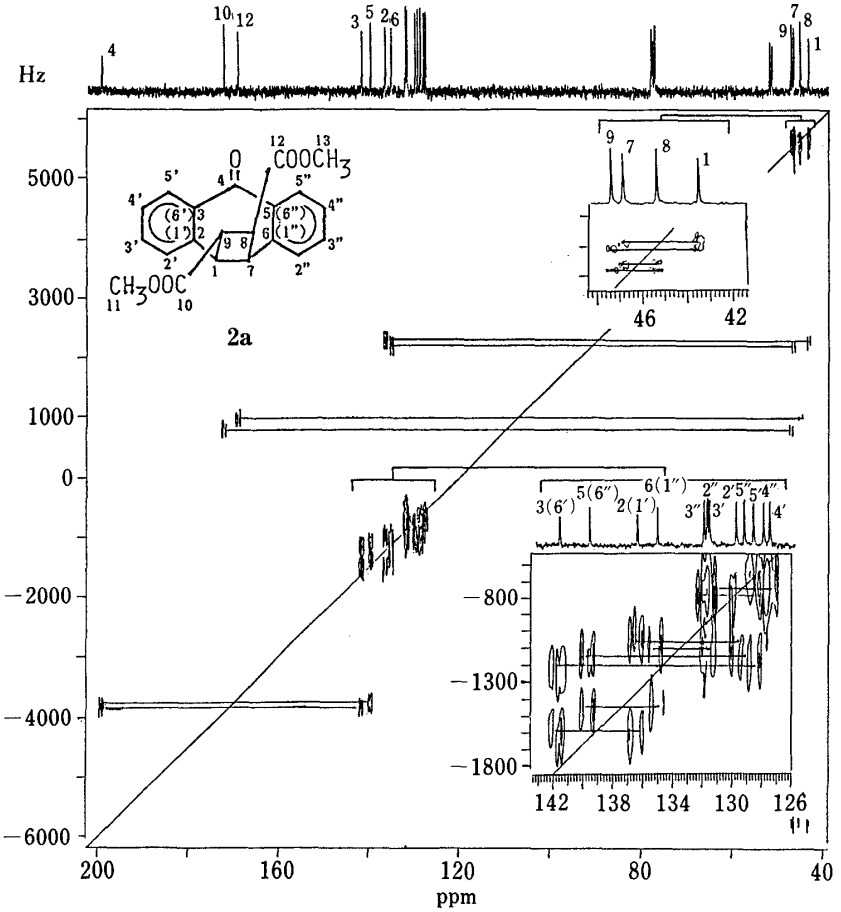


Fig. 2. 2D INADEQUATE Spectra in $CDCl_3$ and Numbering of 8,9-Dimethoxycarbonyl-2 : 3,5 : 6-dibenzobicyclo[5.2.0]nonan-4-one (**2a**)

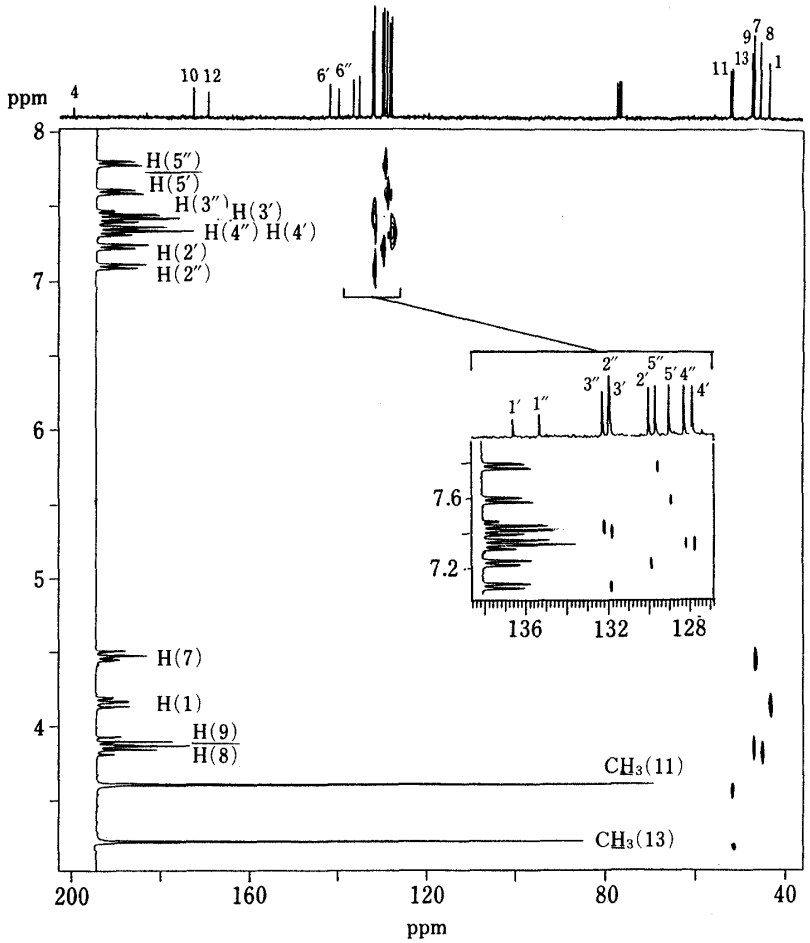


Fig. 3. CH-COSY Spectra of **2a** in $CDCl_3$

C(1)–C(7)–C(8)–C(9)–C(1), for benzene rings, –C(2′)–C(1′)–C(6′)–C(5′)– and –C(2″)–C(1″)–C(6″)–C(5″)–, and for the esteric carbonyl groups C(10)–C(9)–C(8)–C(12) were apparent. Unfortunately, the carbon–carbon connectivities between C(2′)–C(3′), C(5′)–C(4′), C(2″)–C(3″), and C(5″)–C(4″) in the benzene-ring carbons could not be established because of the highly AB character of these resonance pairs. The assignments for these carbons were determined from CH-COSY spectra (Fig. 3). Here, the proton coupling networks in the benzene rings were determined by ordinary selective proton-decoupling (^{1}H–{^{1}H}-NMR), and/or COSY[9] (not shown) experiments. The conventional ^{1}H–{^{1}H}-NMR experiments revealed the sequence of protons, that is, H(2′)–H(3′)–H(4′)–H(5′) and H(2″)–H(3″)–H(4″)–H(5″). The same conclusion was obtained from COSY spectra. The CH-COSY experiments, then, established connectivities between directly bonded ^{13}C and ^{1}H nuclei in the benzene rings. Connectivities between carbonyl (C(10), C(12)) and methoxyl groups were established by the low-power selective ^{1}H decoupled ^{13}C-NMR experiments on irradiating the methyl protons of the methoxyl groups. Low-power irradiation of the proton resonance at δ 3.22, decoupled the ^{13}C signal at δ 169.27 more effectively than that at δ 172.56. On the contrary, irradiation of the resonance at δ 3.61, decoupled the ^{13}C signal at δ 172.56 more effectively than that at δ 169.27.

In this way, we could obtain unambiguous total carbon and proton assignments of **2a**. Thus, the structure of **2a** was confirmed. Observed ^{13}C and ^{1}H chemical shifts, their assignments, and ^{1}H–^{1}H coupling constants are listed in Table II.

As a next step, the stereostructure of **2a** has been studied by measuring the ^{1}H–^{1}H

TABLE II. Final Assigned ^{13}C and ^{1}H Signals, and Proton–Proton Coupling Constants for **2a** in $CDCl_3$

Carbon[a]	^{13}C chemical[b] shifts (δ)	^{1}H chemical[b] shifts (δ)	^{1}H–^{1}H coupling[c] constants (Hz)
1	43.41	4.16	(9.1, 11.2)[e]
2 (1′)	136.51		
3 (6′)	141.87		
4	199.48		
5 (6″)	139.91		
6 (1″)	135.21		
7	46.79	4.48	(9.1, 9.8, 0.9)[e]
8	45.35	3.84	(9.8, 9.8)[e]
9	47.23	3.89	(9.8, 11.2, 0.9)[e]
10	172.56		
11	52.01	3.61	
12	169.27		
13	51.60	3.22	
2′	129.88	7.23	7.4, 1.4
3′[d]	131.76	7.41	7.4, 7.5,[f] 1.4
4′[d]	127.75	7.325	7.4, 7.5,[f] 1.4
5′	128.90	7.58	7.4, 1.6
2″	138.13	7.10	7.6, 1.4
3″[d]	132.12	7.44	7.6, 7.5,[f] 1.4
4″[d]	128.18	7.331	7.6, 7.5,[f] 1.4
5″	129.56	7.77	7.6, 1.6

a) Labelling as shown in Fig. 2. *b*) In ppm relative to internal $^{13}CH_3Si(CH_3)_3$, ±0.002 ppm in ^{1}H and ±0.015 ppm in ^{13}C. *c*) ±0.10 Hz in $CDCl_3$, ±0.25 Hz in DMSO-d_6. *d*) Obtained from CH-COSY spectra coupled with consideration of ^{1}H–^{1}H coupling networks. *e*) Obtained from ^{1}H-NMR spectra in DMSO-d_6. *f*) Inaccurate.

NOE[10] among the protons in **2a**, since intramolecular NOE can give good information on the conformation and configuration of molecules in solution. The NOE experiments were performed at 21 °C in dimethyl sulfoxide-d_6 (DMSO-d_6) and also at 10 °C in $CDCl_3$. The solvents were chosen to separate the proton signals to be discussed and the temperature was varied to inquire into the effect of the molecular motion on the NOE. Observed NOE difference spectra and NOE values (%) are shown in Figs. 4 and 5, and Table III.

As shown in Figs. 4c and d, irradiation at the resonances due to H(1) and H(8) produced NOEs for all the remaining three protons in the cyclobutane ring[11] of **2a** (Table III). In contrast, irradiation at the H(7) resonance produced NOEs for H(1) and H(8), but not for H(9), which takes a 1,3-related position with respect to the irradiated proton. Since the observed NOE values between H(1)–H(7) (9—11%) and H(7)–H(8) (10—17%) are much larger than that between H(1)–H(9) (4.4%) or H(8)–H(9) (3.6%), H(1), H(7) and H(8) of the cyclobutane ring can be considered to take a *cis* arrangement with respect to each other and H(9) to take a *trans* arrangement about these three protons. This *trans* relation between H(9) and the remaining three protons is supported by ^{13}C–{^{1}H} NOE measurements described later. Observed Overhauser effects between H(1)–H(2′) (19.5%) and H(7)–H(2″) (19.2%) were very large. This indicates that the distance between benzene protons (H(2′) and H(2″)) and cyclobutane protons (H(1) and H(7)) is very short.

NOE measurements between methyl protons (δ 3.22 and 3.61) and benzene protons were also made at 10 °C in $CDCl_3$. These results are shown in Fig. 5 and Table III. When the high-field methyl proton resonance at δ 3.22 was irradiated, small Overhauser effects were observed on H(5″) (1.2%), H(3″) (1.3%), H(4″) (1.3%), and H(2″) (1.2%) in the benzene ring (Fig. 5c).

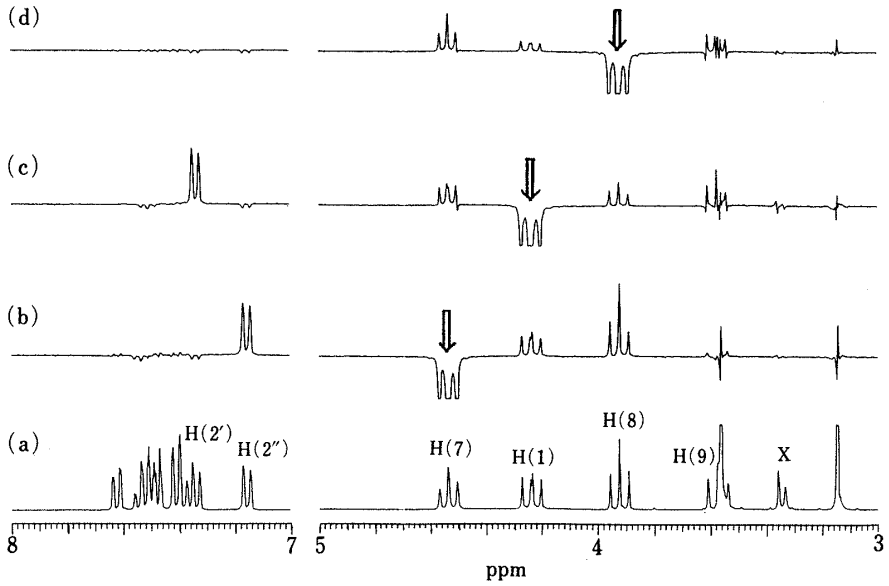


Fig. 4. NOE Spectra of **2a** in DMSO-d_6 at 21 °C

(a) Off-resonance decoupled spectrum; (b), (c), (d) NOE difference spectra between off- and on-resonance (shown by arrow) saturated.

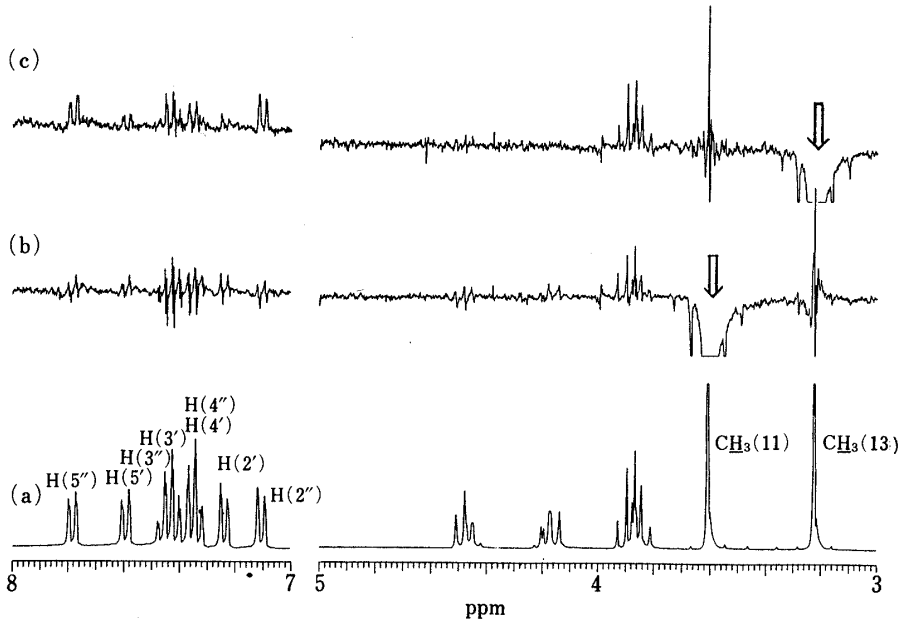


Fig. 5. NOE Spectra of **2a** in $CDCl_3$ at 10 °C

(a) Off-resonance decoupled spectrum; (b), (c) NOE difference spectra between off- and on-resonance (shown by arrow) saturated.

On the other hand, no NOE was detected between the low-field methyl proton at δ 3.61 and the benzene ring protons (Fig. 5b). These results indicate that the higher-field methyl proton is closer to the benzene ring than the lower one. This view is also supported by the large difference (0.4 ppm) in the chemical shifts between the two methyl proton resonances which may be ascribable to the ring current effect of the aromatic ring planes.[6]

In order to obtain more direct information on the steric arrangement of C(9), we measured ^{13}C–$\{^1H\}$ NOEs.[12] The results are shown in Table IV. The ^{13}C–$\{^1H\}$ NOE experiments show that H(1) of **2a** is close to the esteric carbonyl C(10) which is attached to

TABLE III. NOE in **2a**

Solvent	Irradiated	Observed	Percentage of enhancement
DMSO-d_6 at 21 °C	H(1)	H(7)	9.2
		H(8)	6.2
		H(9)	4.4
		H(2′)	19.6
	H(7)	H(1)	11.2
		H(8)	16.5
		H(2″)	19.2
	H(8)	H(1)	4.5
		H(7)	9.5
		H(9)	3.6
$CDCl_3$ at 10 °C	H(13)	H(2″)	1.2
		H(3″)	1.3
		H(4″)	1.3
		H(5″)	1.2

TABLE IV. ^{13}C–{^1H} NOE in **2a**

Observed	Irradiated		
	H(1)	H(7)	H(8), H(9)
C(4)	1.03	1.01	1.11
C(2)	1.23	1.02	1.12
C(6)	1.04	1.27	1.10
C(10)	1.29	0.97	1.86
C(12)	1.01	0.96	1.51

The NOE values listed by the ratio of the signal intensity of on- to off-resonance decoupled spectra in absolute intensity mode. Average error ± 0.05.

C(9), and H(9) is close to the carbonyl carbon C(4). These results confirm that the proton which is attached to C(9) in *endo*-form takes a *trans* position about the three protons of the same cyclobutane ring. Then, taking the confirmation into account, it can be rationally considered that the reaction of **2a** with NaH at 60 °C proceeded to afford **6a** as a major product in high yield, that is, **6a** was formed by removing the H(8) methine proton in **2a** and by inverting the configuration of the methoxycarbonyl group together with transannular bridging of C(4) and C(8).

Consequently, the NOE experimental data indicate that the three cyclobutane protons (H(1), H(7) and H(8)) are in *cis* configuration with respect to each other and H(9) is in *trnas*. Moreover, the distances between H(2′) and H(1) and between H(2″) and H(7) are very short, H(9) is spatially close to C(4), and the methyl group which resonates at a higher field is located at the upper area of the benzene ring plane. Taking into consideration the stereomodel based on the NOE results, the configuration and conformation of **2a** should be A-form, as shown in Fig. 1.

In conclusion, stereochemically interesting adducts (**2a** and **3a**) were prepared by the photocycloaddition reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with dimethyl maleate or fumarate and the adducts were treated with base to afford isomeric compounds (**4a**, **5a**, **6a**, and **7a**).

In order to obtain an unambiguous structural assignment of **2a**, 2D NMR (2D INADEQUATE and CH-COSY) and NOE experiments were undertaken. It was concluded

that **2a** has a *cis* ring juncture and *trans* configuration of two methoxycarbonyl groups and that the seven-membered ring has a boat conformation (A-form as indicated in Fig. 1). However, sufficient evidence to discuss the steric structures of **3a**, **4a**, and **5a** has not yet been obtained. The results on these compounds will be described in the next report.

Experimental

All melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-420 spectrophotometer and ultraviolet (UV) spectra on a Shimadzu UV-200 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian CFT-20 FTNMR spectrometer operating at 80 MHz (^{1}H) and at 20 MHz (^{13}C). The spectra were taken at a pulse flip angle of 20—35° with 8 k words memory for 1000- (^{1}H) or 4500 Hz (^{13}C) spectral widths. Chemical shifts were determined in ppm from tetramethylsilane (TMS) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. MS were obtained on a Hitachi M-80 mass spectrometer with a direct inlet system operating with an ionization energy of 20 eV.

All the ^{13}C (75.4 MHz) and ^{1}H (300.0 MHz) NMR spectra of **2a** were obtained on a Varian XL-300 spectrometer using a 5 mm broad-band probe and operating in a pulse Fourier-transform mode with quadrature detection. The software used to obtain 2D NMR spectra was from Varian Instruments, version 5.2 and/or 6.1. All spectra except 2D ^{13}C–^{13}C double quantum (2D INADEQUATE) spectra were recorded for $CDCl_3$ and DMSO-d_6 solutions which contained 70 mg of sample in 0.6 ml of solvent which included TMS as an internal reference. The 2D INADEQUATE spectra were recorded for saturated solutions of $CDCl_3$ containing **2a** (*ca.* 200 mg/0.6 ml) and 3% by weight of chrom(III)–acetylacetonate (Merck) as a relaxation reagent.

The 2D INADEQUATE experiments were performed using the pulse sequence[7a] which applies a final detection pulse (read pulse) of 135°[7] with a 32 phase cycling.[13] Broad band decoupling was applied continuously. The spectra were collected as 64 × 4k or 64 × 1k (for the cyclobutane region) data points which were zero filled during processing to give 256 × 2k or 256 × 1k real points. The first dimension free induction decaies (FID(s)) were weighted by an exponential line broadening function of 4 or 5 Hz; double quantum dimension interferograms were weighted by that of 40 or 7 Hz. Digital resolutions were 6.0 or 2.0 Hz in the chemical shift dimension and 48.0 or 3.9 Hz in the double quantum frequency dimension. The 2560 or 1280 increments were acquired with a preparation delay of 1.5 s; the total acquisition times were 76 and 42 h, respectively. The timing of the INADEQUATE sequence was calculated and set by the 2D INADEQUATE program of the XL-300 spectrometer, based on $^1J_{C-C}$ coupling of 42 or 39 Hz.

The 2D CH-COSY experiments were performed using the pulse sequence with a 16 phase cycling to provide quadrature detection in both frequency dimensions.[8] The spectra were collected as 128 × 2k or 64 × 1k (for the aromatic region) data points and were processed by using double exponential apodization functions (Gaussian apodization function) prior to Fourier transformation in both dimensions with zero filling to give 256 × 1k or 256 × 512 real data points. Digital resolutions were 12.5 Hz in ^{13}C and 5.8 Hz in ^{1}H dimensions or 2.2 Hz in ^{13}C and 1.0 Hz in ^{1}H dimensions.

The COSY[9] spectra were acquired as 128 × 1k or 64 × 1k (for the aromatic proton region) data points and were transformed by using a pseudo echo function[14] for both frequency dimensions with zero filling to give 512 × 512 or 256 × 256 real data points. The final data matrix was symmetrized[15] prior to plotting. Digital resolutions were 3.2 and/or 1.8 Hz per point in both dimensions.

The ^{1}H–^{1}H NOE experiments in the difference mode[10c,16] were performed at 21 °C for DMSO-d_6 solutions and at 10 °C for $CDCl_3$ solutions. Eight transients were acquired by irradiating the on-resonance position of a spin to be saturated and then eight transients were acquired by irradiating at an off-resonance position. This cycle was repeated eight times for $CDCl_3$ solutions and 32 times for DMSO-d_6 solutions. The total FID obtained by off-resonance irradiation was subtracted from the total FID obtained by on-resonance irradiation and the resultant FID was Fourier-transformed. The NOE is the ratio of the intensity (integral values) of a signal to that of the irradiated one in the difference spectrum. The decoupling power ($\gamma H_2/2\pi$) was 4 Hz.[17] Saturating power was turned off during acquisition so that coupled spectra were obtained. Saturation and acquisition times were 6 and 5 s, respectively.

The ^{13}C–{^{1}H} NOE experiments for $CDCl_3$ solution of **2a** at 23 °C were performed by a similar procedure to that used for the ^{1}H–^{1}H NOEs. However, the cycle was 80 times; the NOE is the ratio of the signal intensity of on- to off-resonance spectrum; the decoupling power ($\gamma H_2/2\pi$) was 11 Hz; saturation and acquisition times were 30[12b] and 1.2 s, respectively. Confirmation of the NOEs was also made in the difference spectrum (not shown).

The selective ^{1}H-decoupled ^{13}C-NMR spectra were observed for $CDCl_3$ solutions. Digital resolution was 0.41 Hz per point. Decoupling power ($\gamma H_2/2\pi$) was 53.0 Hz.

8,9-Dimethoxycarbonyl-2:3,5:6-dibenzobicyclo[5.2.0]nonan-4-one (2a and 3a)——A solution of 5*H*-dibenzo[*a*,*d*]cycloheptatrien-5-one (**1**) (5.6 g) and dimethyl maleate (37 ml) or dimethyl fumarate in dioxane (140 ml) was externally irradiated with a 100 W high-pressure Hg lamp under N_2 in a quartz or Pyrex vessel for 20—30 h. After removal of the solvent, excess of dimethyl maleate and other components by distillation *in vacuo*, the residue

was solidified. Recrystallization from EtOH gave **2a** as colorless needles, mp 154—156 °C, in 75—80% yield. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.30; H, 4.98. UV λ_{max}^{EtOH} nm (log ε): 270 (4.03). After removal of the crystals, the mother liquor was concentrated to give another product (**3a**) as colorless prisms (recrystallized from EtOH), mp 134—136 °C, in 7—8% yield. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.25; H, 5.20. UV λ_{max}^{EtOH} nm (log ε): 267 (4.04).

Reaction of 2a with Bases

a-i) With NaH at 80 °C——NaH (50%, 140 mg, washed with *n*-hexane) was added to a stirred solution of **2a** (1.0 g) in anhydrous DMF (7 ml) and the mixture was stirred at 80 °C under N_2 for 20 min and then at room temperature for 1 h. The resulting solution was poured into ice-water (50 ml), then the precipitate was collected by filtration. Recrystallization from EtOH gave 326 mg of 8,9-dimethoxycarbonyl-2 : 3,5 : 6-dibenzobicyclo[5.2.0]nonan-4-one (**4a**) as faintly yellow prisms, mp 178—179 °C. *Anal.* Calcd for $C_{21}H_{18}H_5$: C, 71.99; H, 5.18. Found: C, 72.17; H, 5.19. UV λ_{max}^{EtOH} nm (log ε): 270 (4.19).

The aqueous solution, which was obtained after removal of the precipitate, was acidified with 10% HCl and extracted with ether. The extract was washed with aqueous saturated NaCl solution and dried over Na_2SO_4. The concentrated ethereal solution was treated with CH_2N_2–ether and the resulting solution was kept standing for 2—3 h to give 218 mg of additional **4a**. The mother liquor was concentrated and the residual solid was recrystallized from EtOH to give 88 mg of 8,9-dimethoxycarbonyl-4-hydroxy-2 : 3,5 : 6-dibenzotricyclo[5.2.0.$0^{4,8}$]nonane (**6a**) as colorless fine needles, mp 210—212 °C. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.22; H, 5.04. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (free OH), 3425 (assoc. OH). UV λ_{max}^{EtOH} nm (log ε): 240 (3.85), 272.5 (3.20), 280 (3.14). After removal of the crystals, the mother solution was concentrated to give 178 mg of another 8,9-dimethoxycarbonyl-4-hydroxy-2 : 3,5 : 6-dibenzotricyclo[5.2.0.$0^{4,8}$]nonane (**7a**) as colorless needles (recrystallized from EtOH), mp 155—157 °C. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.72; H, 5.11. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH). UV λ_{max}^{EtOH} nm (log ε): 241 (3.89), 272 (3.13), 279 (3.07).

a-ii) With NaH at 60 °C——NaH (50%, 140 mg, washed with *n*-hexane) was added to a stirred solution of **2a** (1 g) in anhydrous DMF (7 ml) and the mixture was stirred at 60 °C under N_2 for 20 min and at room temperature for 1 h. The solution was treated in the same manner as in the case of a-i) to give 606 mg of **6a** and 40 mg of **4a**.

b) With KOH——A mixture of **2a** (1.0 g), KOH (2.0 g), EtOH (18 ml), and water (2 ml) was heated under reflux for 5 h. After removal of the solvent by evaporation *in vacuo*, the residue was dissolved in a small amount of water and acidified with 10% HCl. The precipitate was extracted with ether. The extract was washed with aqueous saturated NaCl solution, dried over Na_2SO_4 and concentrated. The concentrated ethereal solution was treated with CH_2N_2–ether and the resulting solution was kept standing for 2—3 h to give 399 mg of **4a**. The mother solution was concentrated and the residual solid was purified by recrystallization from EtOH to give 135 mg of **6a**, 102 mg of **4a**, and 40 mg of another 8,9-dimethoxycarbonyl-2 : 3,5 : 6-dibenzobicyclo[5.2.0]nonan-4-one (**5a**) as faintly yellow prisms, mp 192—193 °C. *Anal.* Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.32; H, 5.18. UV λ_{max}^{EtOH} nm (log ε): 270 (4.17).

Reaction of 3a with Bases

a) With NaH——Treatment of **3a** (200 mg) with NaH in the same manner as in the case of a-i) gave 5 mg of **4a**, 80 mg of **6a**, and 6 mg of **7a**. Compounds **4a**, **6a**, and **7a**, were identified by IR and ^{1}H-NMR spectroscopy.

b) With KOH——A mixture of **3a** (350 mg), KOH (700 mg), EtOH (5.6 ml), and 1.4 ml of water was heated under reflux for 1 h. After removal of the solvent by evaporation *in vacuo*, the residue was dissolved in a small amount of water and acidified with 10% HCl. The precipitate was collected by filtration and washed with ether. A solution of the precipitate in MeOH was treated with CH_2N_2–ether to give 208 mg of the starting material **3a**. The aqueous layer was extracted with ether. The washed and extracted ethereal solutions were combined, washed with aqueous saturated NaCl solution, dried over Na_2SO_4 and concentrated. The solution was treated with CH_2N_2 and purified in the case of b) (**2a** with KOH) to give 28 mg of **6a**, 0.5 mg of **4a** and 10 mg of **5a**. Compounds **6a** and **5a**, were identified by IR and ^{1}H-NMR spectrometry.

Hydrolysis of 2a with Na_2CO_3——A mixture of **2a** (3.0 g) and Na_2CO_3 (1.5 g) in MeOH (30 ml) and water (30 ml) was heated under reflux for 20 min and the solvent was evaporated off *in vacuo*. The residual mass was dissolved in a small amount of water and acidified with 10% HCl, then the resulting precipitate was collected by filtration. Recrystallization of the product from acetone–water gave 2.78 g of the monoacid (**2b**) as colorless needles, mp 224—226 °C. *Anal.* Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.70; H, 4.58. IR ν_{max}^{KBr} cm^{-1}: 3000—2400 (COOH), 1740, 1705, 1650 (CO). ^{1}H-NMR ($CDCl_3$–DMSO-d_6) δ: 3.20 (3H, s, C$\underline{H}_3$), 3.7—4.6 (4H, m, cyclobutane H), 6.3 (1H, br, COOH), 6.95—7.8 (8H, m, arom. H).

Hydrolysis of 7a with Na_2CO_3——A mixture of **7a** (200 mg), Na_2CO_3 (100 mg), MeOH (2 ml) and water (2 ml) was heated under reflux for 20 min and treated in the same manner as in the case of **2a** to give the monoacid (**7b**) as colorless prisms, mp 191—192 °C (recrystallized from ether), in a quantitative yield. *Anal.* Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.63; H, 4.86. IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 3000—2400 (COOH), 1720 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.26 (3H, s, C$\underline{H}_3$), 3.8—4.2 (3H, m, cyclobutane H), 4.54 (2H, br, O$\underline{H}$, COO$\underline{H}$), 6.8—7.1 (8H, m, arom. H).

Hydrolysis of 5a with Na_2CO_3——A suspension of **5a** (200 mg), Na_2CO_3 (300 mg), MeOH (6 ml) and water

(6 ml) was heated under reflux for 25 min and treated in the same manner as mentioned above to give 144 mg of the monoacid (**5b**) as colorless needles, mp 219—220 °C (recrystallized from EtOH). *Anal.* Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.45; H, 4.80. IR ν_{max}^{KBr} cm^{-1}: 3000—2400 (COOH), 1750, 1705, 1640 (CO). ^{1}H-NMR ($CDCl_3$) δ: 3.64 (3H, s, C<u>H</u>$_3$), 3.70—4.10 (3H, m, cyclobutane H), 4.79 (1H, t-like, cyclobutane H), 7.07 (1H, m, arom. H), 7.15—7.60 (5H, m, arom. H), 7.90 (1H, m, arom. H), 8.26 (1H, m, arom. H), 8.86 (1H, br, COO<u>H</u>).

Hydrolysis of 6a with Na_2CO_3——A mixture of **6a** (200 mg), Na_2CO_3 (150 mg), MeOH (3 ml) and water (3 ml) was heated under reflux for 20 min and treated in the same manner as mentioned above. Recrystallization of the resulting precipitate from acetone–water gave 87 mg of a monoacid as colorless needles, mp 224—226 °C, undepressed on admixture with **2b**.

General Method for Hydrolysis of 2a—7a with KOH——A mixture of **2a—7a** and 10% KOH–EtOH was stirred at room temperature (r.t.) for 1—2 h or heated under reflux (refl.) for a short time. After removal of the solvent by evaporation *in vacuo* below 30 °C, the residue was dissolved in a small amount of water and acidified with 10% HCl to give the corresponding dicarboxylic acid.

Product	mp (°C) (Recryst. solv.)	Reaction condn.	Formula	Analysis (%) Calcd (Found) C	H	Yield (%)
2c	187—189 (H_2O)	r.t.	$C_{19}H_{14}O_4$	70.80 (70.44	4.27 4.31)	Quant.
3c	253 (dec.) (MeOH–H_2O)	r.t.	$C_{19}H_{14}O_5$	70.80 (70.79	4.28 4.15)	94
4c	250 (Et_2O)	refl.	$C_{19}H_{14}O_5 \cdot H_2O$	67.05 (66.81	4.75 4.45)	Quant.
5c	240 (dec.) (Acetone)	refl.	$C_{19}H_{14}O_5$	70.80 (70.88	4.28 4.20)	Quant.
6c	260—263 (dec.) (H_2O)	r.t.	$C_{19}H_{14}O_5$	70.80 (70.92	4.28 4.17)	82
7c	118—121 (Et_2O–*n*-hexane)	refl.	$C_{19}H_{14}O_5 \cdot C_4H_{10}O$	69.68 (69.64	6.10 6.00)	Quant.

Reduction of 2a——$NaBH_4$ (1.4 g) was added portionwise to a stirred suspension of powdered **2a** (1.0 g) in MeOH (30 ml) for 40 min at room temperature and then the mixture was stirred for 1 h. After removal of the solvent by evaporation *in vacuo*, the residue was poured into ice-water and extracted with ether. The ethereal extract was washed with aqueous saturated NaCl solution, dried over Na_2SO_4 and concentrated to give 713 mg of the diol (**8**) as colorless prisms, mp 172—174 °C. *Anal.* Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.01; H, 6.23. IR ν_{max}^{KBr} cm^{-1}: 3375 (OH), 1700 (ester CO). ^{1}H-NMR ($CDCl_3$) δ: 1.7 (2H, br, O<u>H</u> × 2), 3.44 (3H, s, C<u>H</u>$_3$), 3.5—4.0 (5H, m, >C<u>H</u>$_2$, cyclobutane H), 4.51 (1H, t-like, cyclobutane H), 5.94 (1H, br s, >C<u>H</u>O–), 6.85 (1H, m, arom. H), 7.0—7.25 (5H, m, arom. H), 7.35—7.6 (2H, m, arom. H). ^{13}C-NMR (DMSO-d_6) δ: 39.6, 40.3, 41.3, 42.3 (four cyclobutane carbon), 51.0 (<u>C</u>H$_3$), 63.3 (–<u>C</u>H$_2$–), 67.7 (><u>C</u>HO–), 173.9 (–<u>C</u>OO–).

The Lactone (9)——NaH (50%, 90 mg, washed with *n*-hexane) was added to a stirred solution of the diol (**8**) (500 mg) in anhydrous DMF (5 ml) under ice-cooling and N_2, and the mixture was stirred for 15 min. A solution of tosyl chloride (300 mg) in DMF (2 ml) was added to the solution under the same conditions and the mixture was stirred for 20 min. The reaction mixture was poured into 60 ml of ice-water and acidified with 10% HCl, then the precipitate was collected by filtration. Recrystallization from acetone gave 275 mg of the lactone (**9**) as colorless prisms, mp 275—278 °C. *Anal.* Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.27; H, 5.52. IR ν_{max}^{KBr} cm^{-1}: 3525, 3450 (OH), 1745 (lactone CO). ^{1}H-NMR ($CDCl_3$) δ: 1.64 (1H, br, O<u>H</u>), 3.35—3.75 (2H, m, cyclobutane H), 4.21 (2H, m, cyclobutane H or –C<u>H</u>$_2$–), 4.61 (2H, m, –C<u>H</u>$_2$– or cyclobutane H), 6.12 (1H, s, >C<u>H</u>O–), 6.90 (1H, m, arom. H), 7.05—7.3 (5H, m, arom. H), 7.64 (2H, m, arom. H). ^{13}C-NMR (DMSO-d_6) δ: 38.6, 39.2, 42.5, 43.3 (four cyclobutane C), 67.6 (><u>C</u>HO–), 73.2 (><u>C</u>H$_2$–), 179.6 (–<u>C</u>OO–).

Reduction of 3a——$NaBH_4$ (55 mg) was added to a stirred suspension of powdered **3a** (100 mg) in 90% MeOH (3 ml) at room temperature and the mixture was stirred for 25 min. The reaction mixture was neutralized with diluted HCl. After removal of the solvent by evaporation *in vacuo*, the precipitate was collected by filtration and washed with water. Recrystallization of the product from EtOH gave 95 mg of the corresponding alcohol (**10**) as colorless leaflets, mp 165—165.5 °C. *Anal.* Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.77; H, 5.64. IR ν_{max}^{KBr} cm^{-1}: 3225 (OH), 1730 (ester CO). ^{1}H-NMR ($CDCl_3$) δ: 2.63 (1H, br, O<u>H</u>), 3.79 (6H, s, C<u>H</u>$_3$ × 2), 3.79 (2H, m, cyclobutane H), 4.42 (2H, m, cyclobutane H), 6.12 (1H, s, >C<u>H</u>O–), 6.7—7.25 (6H, m, arom. H), 7.4—7.65 (2H, m, arom. H).

Reduction of 4a——i) Powdered **4a** (150 mg) in MeOH (30 ml) and water (20 ml) was treated with $NaBH_4$ (80 mg) in the same manner as mentioned above to give 139 mg of the corresponding alcohol (**11a**) as an amorphous

solid. IR ν_{max}^{KBr} cm^{-1}: 3475 (OH), 1740, 1720 (ester CO). ^{1}H-NMR ($CDCl_3$) δ: 2.17 (1H, br, OH), 3.42 (1H, m, cyclobutane H), 3.55—3.8 (2H, m, cyclobutane H), 3.75 (3H, s, CH_3), 3.80 (3H, s, CH_3), 4.54 (1H, m, cyclobutane H), 5.71 (1H, s, >CHO–), 7.1—7.95 (8H, m, arom. H).

A solution of **11a** in pyridine was treated with acetic anhydride in a usual manner to give a sole product (**11b**) as colorless prisms (recrystallized from EtOH), mp 148—150 °C, in a good yield. *Anal.* Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.12; H, 5.55. IR ν_{max}^{KBr} cm^{-1}: 1735 (CO). ^{1}H-NMR ($CDCl_3$) δ: 1.94 (3H, s, CH_3CO), 3.33 (1H, m, cyclobutane H), 3.55—3.90 (2H, m, cyclobutane H), 3.79 (3H, s, CH_3), 3.81 (3H, s, CH_3), 4.42 (1H, m, cyclobutane H), 7.02 (1H, s, >CHO–), 7.1—7.5 (8H, m, arom. H).

ii) A suspension of **4a** in MeOH was catalytically hydrogenated over PtO_2 at room temperature under atmospheric pressure and the resulting solution was treated in a usual manner to give **11a** as a sole product in good yield.

Reduction of 5a——Powdered **5a** (150 mg) in MeOH (18.5 ml) and water (1.3 ml) was treated with $NaBH_4$ (94 mg) in the same manner as mentioned above to give 140 mg of a mixture of epimeric alcohols (**12**) as faintly yellow prisms (recrystallized from ethyl acetate–*n*-hexane), mp 143—150 °C. *Anal.* Calcd for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.58; H, 5.80. IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 1740, 1720 (ester CO). ^{1}H-NMR ($CDCl_3$) δ: 3.62 (s, CH_3), 3.69 (s, CH_3), 3.73 (s, CH_3), 3.74 (s, CH_3), 3.4—4.0 (m, cyclobutane H), 4.6 (m, cyclobutane H), 5.64 (s, >CHO–), 6.60 (s, >CHO–), 6.8—7.7 (m, arom. H).

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References and Notes

1) This paper follows a previous report entitled "Synthesis of 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene Derivatives," see ref. 2. A part of this work was presented at the Kinki Regional Meeting of the Pharmaceutical Society of Japan, Kobe, November 1981.
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