Substituent Effects for the Benzene Ring on Solvolysis of 3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-yl *p*-Nitrobenzoate

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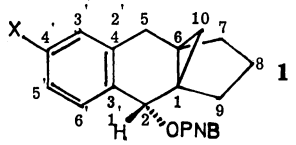
Preparations of *anti*-4′-substituted 3,4-benzotricyclo[4. 3. 1. 0^{1,6}]dec-3-en-2-yl *p*-nitrobenzoates (**1a—d**) are described. The solvolysis of these esters was examined in 80% aqueous acetone. The rates were relatively high but the sensitivity to substituents on the benzene ring was low in comparison with other secondary systems. It is considered that σ-participation rather than π-conjugation might contribute to the rate accelerative effect. In the presence of a base, **1a—d** gave *anti*-alcohol (**12a—d**) (13 to 17%), *syn*-alcohol (**13a—d**) (31 to 78%), and *tert*-alcohol (**14a—d**) (5 to 54%). The product distributions are explained in terms of a nonclassical homonaphthalenium cation (**24**).

There is abundant experimental evidence for selective product formation,[1] rate acceleration,[1a,1b,2] and transmittance of the substituent effect[3] in the solvolysis of various types of substrates in which bent, electron-releasing systems like cyclopropyl groups are situated at the reaction center.[4] The remarkable effect of the cyclopropyl group in stabilizing an adjacent carbocation is well documented for a large number of solvolyses.[1,2,4] Also, a π-electron system such as a phenyl or a vinyl group is similarly capable of conjugation with an adjacent cationic center.[5]

Deno *et al.*[6] and Brown *et al.*[7] reported that a cyclopropyl group contributes to stabilization of the cationic center to a greater extent than does a phenyl group. In contrast, Olah *et al.* reported that the relative effectiveness in delocalizing the positive charge decreases in the following order, Ph>cyclo-C_3H_5>CH_3, on the basis of the ^{13}C chemical shift for the carbocation in various stable species.[8] Then, they suggested that the cyclopropyl group is a more actively participating group in solvolysis than the phenyl group, which delocalizes the charge away from the cationic center better than the cyclopropyl group in the intermediate carbocation.[8] In other words, the effectiveness of charge delocalization (π-conjugation and σ-participation[9,10,17]) by two groups (such π-electron systems as phenyl groups and bent-σ-electron systems as cyclopropyl groups) in the transition state, might be different from that in the intermediate.

These comparisons have been made by studies on the intermolecular competition of different molecules, so that there may be some lack of clarity due to other factors like the steric effect and the solvent effect of the reactivity of the different substrates. The author wishes here to report on the study of the solvolysis of a series of cyclopropylphenylmethyl esters in which the steric environments in the vicinity of the reactive site are essentially identical and a comparison between two substituents can be made intramolecularly.



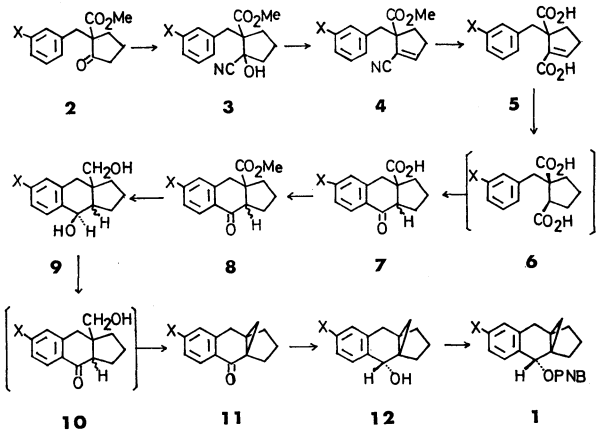
1a X=MeO
1b X=Me
1c X=H
1d X=Cl

Fig. 1. *p*-Nitrobenzoate (**1**).

From a synthesis and solvolytic study of **1c**, it is regarded as a suitable cyclopropylphenylmethyl derivative for examining the above competitive effects.[10] It is now interesting to investigate the substituent effects at the *para*-position of the reactive center of **1** on both the solvolysis rate and the distribution of the solvolysis products. Much information on σ-participation and π-conjugation may be expected from such studies.

Results

Synthesis. Each *p*-nitrobenzoate (**1a—d**) was prepared by the sequence outlined in Scheme 1, which is the same route as in the case of **1c**.[10] 2-(*m*-Substituted benzyl)-2-methoxycarbonylcyclopentanones (**2a—d**)



Scheme 1.

were prepared by the condensation of 2-methoxycarbonylcyclopentanone with *m*-substituted benzyl chloride. The addition of hydrogen cyanide to **2a—d** gave the cyanohydrins (**3a—d**), which were dehydrated by phosphoryl chloride in dry pyridine to afford the unsaturated cyano esters (**4a—d**), and then the unsaturated dicarboxylic acids (**5a—d**) were obtained by the hydrolysis of these cyano esters. Hydrogenation of **5a—d** with Adams' catalyst in ethyl acetate produced the saturated acids (**6a—d**) in high yields. Intramolecular cyclization of **6a—d** with concentrated sulfuric acid gave rise to the keto acids (**7a—d**). Esterification with diazomethane converted **7a—d** almost completely

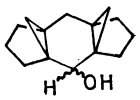
into the esters (**8a—d**) which were reduced by lithium aluminum hydride to give a mixture of at least two diols in good yields, the ratio being about 3: 1 in each case. Contrary to the fact that the above minor products were not oxidized with active manganese dioxide, the oxidation of the major diols (**9a—d**) easily afforded the keto alcohols (**10a—d**). These keto alcohols (**10a—d**) were transformed to their tosylates, followed by heating under reflux in dry pyridine to give the ketones (**11a—d**). Spectroscopic and elemental analyses support the structure of the assigned cyclopropyl phenyl ketones. The NMR spectra of **11a—d** show that the aliphatic proton signals are similar to each other and that each substituent on the benzene ring is at a *para*-position to the carbonyl carbon (Table 5).

Reduction of **11a—d** with lithium aluminum hydride in ether gave the alcohols (**12a—d**), in 85—90% yields, concomitant with a traces of other epimers (**13a—d**) (2—5%). The stereochemical assignment of C_2 (reactive center) is based upon a comparison of the NMR spectra of both epimeric alcohols and upon the inference for the direction of the hydride reduction of **11a—d**. Since it has been confirmed by NMR spectroscopy that a proton which is located above the plane of a cyclopropane ring should be shielded in contrast with a proton in the same plane as that of the cyclopropane, a comparison of the chemical shifts of α-carbinyl protons in two epimers was made.[11] The results are shown in Table 1. As is seen, the *anti* geometry of a hydroxyl group relative to a cyclopropane is assigned to **12a—d**, the main reduction product, in which the α-proton was more shielded, and *vice versa*. The expectation for hydride reduction also leads to the same assignment. It may be expected that the reduction of **11a—d** with lithium aluminum hydride predominantly give the *anti* alcohols (**12a—d**), since the hydride attacks from the less hindered side of the carbonyl group.[12]

Kinetic Studies. The rates of solvolysis of *p*-nitrobenzoates (**1a—d**) were determined by titration of *para*-nitrobenzoic acid in 80% aqueous acetone. The results are summarized in Table 2.

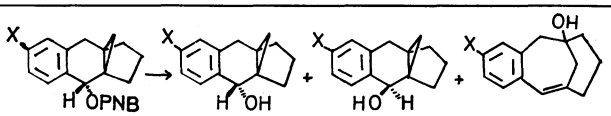
Product Studies. Studies of solvolysis products of **1a—d** were carried out in the presence of 2,6-lutidine. After about ten half-lives, the products were extracted

Table 1. Observed α-hydrogen shifts and their differences due to neighboring cyclopropane

X	Compound	a)	δ[b]	$\Delta\delta$[c]	lit.
MeO	**12a**	*anti*	4.84	0.16	d)
	13a	*syn*	5.00		
Me	**12b**	*anti*	4.83	0.16	d)
	13b	*syn*	4.99		
H	**12c**	*anti*	4.83	0.21	e)
	13c	*syn*	5.04		
Cl	**12d**	*anti*	4.82	0.19	d)
	13d	*syn*	5.01		
		*anti*	3.48	0.69	f)
		syn	4.17		

a) The relation between the OH group and cyclopropane methylene. b) Chemical shifts are given in δ (ppm) relative to the internal reference, tetramethylsilane. c) $\Delta\delta=\delta$ *syn*$-\delta$ *anti*. d) Present study. e) Ref. 10. f) Ref. 11.

Table 3. Product distributions of solvolysis of **1a—d** in the presence of 2,6-lutidine



(1)	(12) %, (δ)[a]	(13) %, (δ)[a]	(14) %, (δ)[a]
1a (X=MeO)	17, (4.84)	78, (5.00)	5, (6.10)
1b (X=Me)	15, (4.83)	46, (4.99)	39, (6.11)
1c[b] (X=H)	13, (4.83)	42, (5.04)	45, (6.17)
1d (X=Cl)	15, (4.82)	31, (5.01)	54, (6.08)
	15±2%[c]	85±2%[c]	

a) (δ): ^{1}H-NMR chemical shifts for characteristic signals in $CDCl_3$ (α-proton of OH-group for **12** and **13**, vinyl proton for **14**) in the solvolysis products.
b) Ref. 10.
c) **13**+**14**/**12**=85±2/15±2=const. The ratio is independent of substituents.

Table 2. Rates of solvolysis of *p*-nitrobenzoate (**1a**, **1b**, **1c**, and **1d**) in 80% aqueous acetone

Compound	T, °C	10^4k, s^{-1}	ΔH^*, kcal/mol	ΔS^*, e.u.	k_{rel}, 25 °C[a]
1a	0.0	1.10 ±0.1			
(X=MeO)	25.0	37.9 ±0.4[b]	22.3	+5.3	44.1[b]
1b	0.0	0.108±0.005			
(X=Me)	25.0	3.22 ±0.1	21.4	−4.7	3.74
1c	25.0	0.860±0.05[c]	20.6	−8.0	1.00
(X=H)	30.0	1.51 ±0.04[c]			
	40.0	4.86 ±0.03[c]			
1d	25.0	0.287±0.021	22.8	−2.9	0.334
(X=Cl)	45.0	3.58 ±0.08			

a) $k_{rel}=k_X/k_H$. The Hammett plots against σ^+ gave an acceptable linear relation ($\rho=-2.11$).
b) Owing to the high reactivity of **1a** (X=MeO), this rate constant at 25 °C may be an upper limit, so that k_{MeO}/k_H is also an upper limit.
c) Ref. 10.

and analyzed using NMR spectroscopy. The product in each series was a mixture of alcohols consisting of **12**, **13**, and **14**, from a comparison of the NMR spectra with those of authentic samples of the **c**-series (X=H).[10] The product distributions were determined from the integral ratio for the characteristic signals in the NMR spectra. The results are summarized in Table 3. The primary alcohols (**15a**—**d**) could not be detected by way of the extraneous singlet signal due to the hydroxymethyl protons in each case.[10]

The following points may be important in the consideration of the reaction intermediate in the solvolysis of **1a**—**d**:

1) The ratio, **13a**—**d**/**12a**—**d**, was varied with the substituent on the benzene ring.

2) Secondary alcohols (**13a**—**d** and **12a**—**d**) increased in the case of the MeO-group, but tertiary alcohols (**14a**—**d**) increased in the case of the Cl-group.

3) The proportions between (**13a**—**d**)+(**14a**—**d**) and (**12a**—**d**) remained almost unchanged with substituent on the benzene ring.

Discussion

Solvolysis Rate. The rate measurements of S_N1 reactions, *i.e.*, the solvolyses of halides, sulfonates and *p*-nitrobenzoates, have been utilized for the purpose of obtaining information as to the factors influencing the stability or the electronic delocalization in an intermediate carbocation for these reactions.[13] A substituent at the *para*-position of a benzene ring in the benzylic substrate does not affect the steric environment near the reactive center, but does affect the ability of electronic conjugation with the site bearing a positive charge in the reaction intermediate.[14] The reaction constant, ρ, in the Hammett equation, or the effect of a single substituent (for instance, k_{MeO}/k_H) may serve for an approximate measure of the variation between the ground state and the transition state on the benzenoid system. Accordingly, the greater the positive charge on the benzene ring at the trasition state in the rate determining step, the greater the rate enhancement provided by *p*-methoxy substitution.

The rate ratios and the rho values obtained in the present study and in certain related systems are listed in Table 4. The rate ratios, k_{MeO}/k_H, for most of these substrates (**16**, **17**, **18**, **20**, and **21**) are fairly large, 0.7—1.5$\times 10^4$, demonstrating that π-conjugation of the intermediate carbocation with the anisyl group contributes considerably to increasing the solvolysis rate, as is generally observed. On the other hand, the rate ratio, 1.4$\times 10^2$, for **19** is rather smaller than the above examples. Since the substituent effect for a highly reactive system like the *tert*-arylmethyl ester is ordinarily smaller, this may be reasonable taking account of the faster rate of **19** by a factor of 10^2—10^4 compared with the other substrates cited above. This is consistent with the postulation that the more stable the carbocation, the less demand for additional stabilization through neighboring group participation.[18] Compared with these values, the ratio, 44, for **1** is the smallest among that for a number of arylmethyl *p*-nitrobenzoates. The relative reactivity of **1** to **19** under the same conditions is about 0.4, namely the reactivity of **1** is similar to or even less than that of **19**, the tertiary ester, but the ratio k_{MeO}/k_H, for **1** is unexpectedly smaller than one half of the ratio for **19**. This is in contrast with the above discussion. This also shows that the conjugative effect of the *p*-MeO-group in **1** might be quite small at the transition state for solvolysis.

On account of the lower rate ratio, k_{MeO}/k_H, and the lower reactivity of this series of compounds, **1**, compared with *tert*-cyclopropylphenylmethyl systems, it is reasonable to assume that the cyclopropane ring is oriented favorably in the 1-bicyclo[3.1.0]hexyl group of **1** against the reactive center and that its bent σ-bond could participate very well to the ionization process in the transition state (σ-participation). As compared with the π-conjugation which stabilizes the intermediate carbocation and reduces the energy of activation in solvolysis indirectly,[19] σ-participation can immediately contribute to the transition state for ionization in solvolysis and might be more effective for the rate than π-conjugation if the stereochemistry is satisfied. This is a result of the present experiments for the rate determination of **1a**—**d** at 25 °C, but for more detail it will be necessary to obtain further thermodynamic parameters such as the enthalpy and entropy of activation.

Recently Eaton and Traylor[20] suggested that the

Table 4. Relative rates (k_X/k_H and k_H/k_{1H}) and reaction constants (ρ) in Hammett's equation of the solvolysis of various *p*-nitrobenzoates in 80% aqueous acetone at 25 °C

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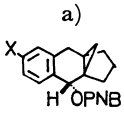
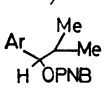
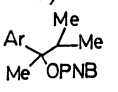
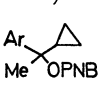
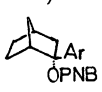
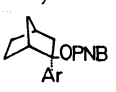
							
	(**1**)	(**16**)	(**17**)	(**18**)	(**19**)	(**20**)	(**21**)
k_{MeO}/k_H	44.1	804	780	686	~137	785.5	1521
k_{Me}/k_H	3.74	2.47	10.9	—	—	—	—
k_{Cl}/k_H	0.334	0.77	0.3	—	—	—	—
ρ[e]	−2.11	—	−3.61	−4.65	−2.78	−3.77	−3.96
$k_{rel.}$	1.0	~10^{-6} [f]	~10^{-2} [f]	1.1$\times 10^{-4}$	2.4	6.2$\times 10^{-4}$	8.8$\times 10^{-2}$

a) Present study. b) Ref. 15. c) Ref. 16. d) Ref. 17.

e) Reaction constant, ρ, in ρ–σ^+ plot.

f) Calculated from data in other solvents (60% aqueous acetone or 65% aqueous dioxane) using the Grunwald-Winstein equation (*Y*-value).

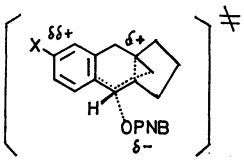
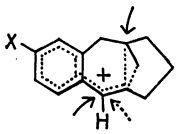


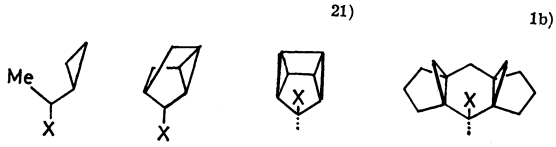
Fig. 2. Transition state in solvolysis of **1**.



(**24**)

Fig. 4. Reaction intermediate in solvolysis of **1**.

rigid cyclopropyl carbinyl system (**23**) affords at least as much stabilization as in the freely rotating system (**22**). However, the model for comparison cited by them is not necessarily a favorable system for solvolysis. A favorable configuration should also be an important factor for vertical stabilization[22] in an electron transition (vertical process) such as Kosower *et al.* have reported.[23]



22 **23**

krel. 1 10^4 10^6

Fig. 3. Relative rates of solvolysis of rigid cyclopropyl systems.

Products. It has been established by Olah *et al.* that the charge density of each carbon atom in a stable carbocation is closely related to their ^{13}C chemical shifts.[24] It is also expected that the above charge distribution resembles, to a certain extent, that of the unstable intermediate ions in solvolysis. They suggested that the π-electron system of the phenyl group, when not hindered by steric effects, can conjugatively delocalize charge more effectively than hyperconjugation with bent C–C bonds.[8] Generally, the distribution of substitution products in solvolysis may depend upon a number of effects, for instance, the charge density and steric factors of the carbon atoms which the solvent attacks.

It may be noted from the present result that the distribution of the hydroxylic products varies considerably with the substituent at the *para*-position of the benzene ring in spite of an almost identical steric environment around the reactive site. The proportions between **13** and **12** changed from 2.1 to 4.6 with various substituents on the benzene ring. Therefore, they are dependent upon the properties of intermediate carbocation rather than the steric factor. These discussions result in the proposition that the intermediate carbocation is essentially not the classical carbocation of the benzyl type. The most remarkable feature is the fact that the proportions between **12** and (**13**+**14**) remain almost constant with the substituents on the benzene ring while the yield for **14** increases from the MeO- to the Cl-group.

The result might be explained on the basis of the formation of an intermediate carbocation in which the positive charge would be highly delocalized not only on the aromatic part but also on the cyclopropane ring as in **24**. Since it is usually recognized that the formation of a bridge-head carbocation in relatively small polycyclic systems is an extraordinarily slow process,[25] the localized or classical C-6 carbocation could be excluded in such reactive species as the present substrates. As the primary homo-allylic alcohols (**15a**—**d**) could not be detected in the product analysis, the positive charge might be delocalized even slightly into the primary carbon (C_{10}) in the intermediate ion (**24**).

In the case of a *p*-MeO-derivative, the positive charge may be principally stabilized by the powerful conjugative effect of the *p*-MeO-group, so that the positive charge density at the C_6 carbon is decreased. This results in the formation of **14** in a low yield in comparison with the other cases. Nevertheless, electron delocalization might expand through C_2–C_1–C_6 to a certain extent and cover the side below this planar ionic species. Consequently, a nucleophilic solvent attack would mostly take place from the upper side of the ion to afford **13** rather than **12** which would be produced by a solvent attack from below. A steric effect around the C_2 position, which does not vary with the substituents on the benzene ring, would have to be incorporated in such a nucleophilic substitution at the C_2 position, but a clear distinction between the effects could not be made in the present study.

As the conjugative effect of a substituent decreases, the positive charge density at the C-6 position might increase proportionately and the ratio of the formation of **14** increase also. If it is assumed that the solvent attack at C_6 and C_2 from the upper side depends substantially on the electron delocalization over the aromatic ring and the C_2–C_1–C_6, plane below which the filled orbital rejects the approach of a nucleophilic solvent molecule, the sum of the two products, **13** and **14**, reflects such electronic circumstances of the intermediate ion (**24**). On the other hand, the solvent attack at C_2 from below would occur responding to the degree that the C_1–C_{10} bonding electrons contribute to this intermediate ion when the steric factors offset each other. It has been reported that nucleophilic solvents enter from the *cis* side to a methylene of the cyclopropane in a large number of solvolyses in which a homo-allylic or homo-aromatic carbocation intervenes.[1b,1c,4,26]

In summary, the rates of solvolysis of **1a**—**d** in 80% aqueous acetone were greatly increased and their sensitivity to a substituent on the benzene ring is small in comparison with other cyclopropylphenylmethyl systems. These results indicate that σ-participation rather than π-conjugation might contribute to the rate accelerative effect due to the earlier transition state in which the hybridization of C_2 (reactive carbon) might not be a complete sp^2-hybridization. On the other hand, in the intermediate, the conjugation between the vacant *p*-orbital at C_2 and the aromatic nucleus

would contribute to the stabilization of the intermediate (**24**). The degree of such stabilization by π-conjugation might be varied with the substituent on the benzene ring.

Experimental

All the melting points are uncorrected. The IR spectra were obtained with a Hitachi 215 grating IR spectrophotometer. NMR measurements were carried out on a Varian T-60 spectrometer, using tetramethylsilane as an internal reference.

The details of synthesis of **1c** will be provided in a future publication.[10]

m-*Substituted Benzyl Chloride.* The chlorides were prepared by the reported methods: *m*-methoxy bp 88—89 °C/4 mmHg (lit,[27] bp 124 °C/13 mmHg), *m*-methyl bp 91—92 °C/22 mmHg (lit,[28] 101—102 °C/30 mmHg), and *m*-chloro derivatives bp 103—105 °C/20 mmHg (lit,[29] 104 °C/17 mmHg).

*2-(*m-*Substituted benzyl)-2-methoxycarbonylcyclopentanone (**2a**, **2b**, and **2d**).* *(a) 2-*m-*Methoxybenzyl-2-methoxycarbonylcyclopentanone (**2a**):* To a suspension of 11 g (0.48 mol) of finely dispersed sodium in 150 ml of dry toluene was added a solution of 69 g (0.48 mol) of 2-methoxycarbonylcyclopentanone[30] in 350 ml of dry benzene with stirring in a nitrogen atmosphere for 2 h. After the mixture was heated under reflux for 2.5 h, a solution of 50 g (0.32 mol) of *m*-methoxybenzyl chloride in 100 ml of dry benzene was added in one portion. Then, the reaction mixture was heated under reflux for 25 h. The usual work-up gave 68 g of colorless **2a** in an 80% yield (bp 189—191 °C/5 mmHg).

*(b) 2-*m-*Methylbenzyl-2-methoxycarbonylcyclopentanone (**2b**):* By a similar method to that used in the preparation of **2a**, **2b** (bp 145—150 °C/2 mmHg, 62 g, 83%) was obtained from *m*-methylbenzyl chloride (78 g, 0.56 mol) and 2-methoxycarbonylcyclopentanone (53 g, 0.38 mol).

*(d) 2-*m-*Chlorobenzyl-2-methoxycarbonylcyclopentanone (**2d**):* By a method similar to that used in the preparation of **2a**, **2d** (bp 173—177 °C/5 mmHg, 88 g, 82%) was obtained from *m*-chlorobenzyl chloride (64 g, 0.4 mol) and 2-methoxycarbonylcyclopentanone (71 g, 0.5 mol).

*2-(*m-*Substituted benzyl)-1-hydroxy-2-methoxycarbonylcyclopentanecarbonitrile (**3a**, **3b**, and **3d**).* *(a) 2-*m-*Methoxybenzyl-1-hydroxy-2-methoxycarbonylcyclopentanecarbonitrile (**3a**):* Into an aqueous solution (150 ml) of sodium cyanide (73 g, 1.5 mol) was added an ethereal solution (90 ml of ether) of **2a** (68 g, 0.26 mol) with vigorous stirring and cooling with ice water. Concentrated hydrochloric acid (82 ml) was added to the above mixture at 5—10 °C; vigorous stirring was continued for 30 h. Crude cyanohydrin (**3a**) (64 g) was obtained in an 85% yield by the ordinary extraction procedure, and used for the following dehydration without further purification. Pure sample, mp 90—98 °C (dec), was obtained by recrystallization from carbon tetrachloride. Found: C, 66.17; H, 6.53; N, 4.87%. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84%.

*(b) 2-*m-*Methylbenzyl-1-hydroxy-2-methoxycarbonylcyclopentanecarbonitrile (**3b**):* By a method similar to that used in the preparation of **3a**, **3b** (mp 105—107 °C (dec), 109 g, 80%) was obtained from **2b** (120 g, 0.49 mol) and sodium cyanide (115 g, 2.4 mol). Found: C, 70.19; H, 6.92; N, 5.15%. Calcd for $C_{16}H_{17}NO_2$: C, 70.31; H, 7.01; N, 5.12%.

*(d) 2-*m-*Chlorobenzyl-1-hydroxy-2-methoxycarbonylcyclopentanecarbonitrile (**3d**):* By a method similar to that used in the preparation of **3a**, **3d** (mp 102—106 °C (dec), 72 g, 73%) was obtained from **2d** (95 g, 0.36 mol) and sodium cyanide (88 g, 1.8 mol). Found: C, 61.52; H, 5.35; N, 4.59; Cl, 12.22%. Calcd for $C_{15}H_{14}NO_2Cl$: C, 61.33; H, 5.49; N, 4.77; Cl, 12.07%.

*5-(*m-*Substituted benzyl)-5-methoxycarbonyl-1-cyclopentenecarbonitrile (**4a**, **4b**, and **4d**).* *(a) 5-*m-*Methoxybenzyl-5-methoxycarbonyl-1-cyclopentenecarbonitrile (**4a**):* To a solution of **3a** (64 g, 0.22 mol) in 220 ml of anhydrous pyridine was added phosphorus oxychloride (100 g, 0.67 mol) with vigorous stirring and cooling below 10 °C. Stirring was continued for 3 h in an ice-water bath, for 12 h at room temperature, and then for 2 h under reflux. After the reaction mixture was poured onto a mixture of crushed ice (100 g) and concd hydrochloric acid (100 ml), 47 g, of **4a** (78% yield) was obtained by the usual work-up; bp 185—190 °C/2 mmHg.

*(b) 5-*m-*Methylbenzyl-5-methoxycarbonyl-1-cyclopentenecarbonitrile (**4b**):* By a method similar to that used in the preparation of **4a**, **4b** (bp 175—184 °C/4 mmHg, 80 g, 89%) was obtained from **3b** (95 g, 0.35 mol) and phosphorus oxychloride (150 g, 1.05 mol).

*(d) 5-*m-*Chlorobenzyl-5-methoxycarbonyl-1-cyclopentenecarbonitrile (**4d**):* The reaction of **3d** (69 g, 0.24 mol) with phosphorus oxychloride (105 g, 0.705 mol) afforded **4d** (bp 192—198 °C/4 mmHg, 55 g, 85%).

*5-(*m-*Substituted benzyl)-1-cyclopentene-1,5-dicarboxylic Acid (**5a**, **5b**, and **5d**).* *(a) 5-*m-*Methoxybenzyl-1-cyclopentene-1,5-dicarboxylic Acid (**5a**).* Hydrolysis of **4a** (38 g, 0.14 mol) was accomplished using 100 ml of concd hydrochloric acid and 50 ml of glacial acetic acid under reflux with stirring for 10 h. The crude **5a** (21 g) was obtained in a 54% yield, and recrystallized from ethyl acetate, mp 196—200 °C. Found: C, 65.09; H, 5.91%. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84%.

*(b) 5-*m-*Methylbenzyl-1-cyclopentene-1,5-dicarboxylic Acid (**5b**):* Crude dicarboxylic acid (**5b**) (34 g) obtained from **4b** (40 g, 0.16 mol) in an 82% yield was recrystallized from ethyl acetate to afford pure **5b**, mp 195—198 °C. Found: C, 69.39; H, 6.18%. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20%.

*(d) 5-*m-*Chlorobenzyl-1-cyclopentene-1,5-dicarboxylic Acid (**5d**):* Hydrolysis of **4d** (44 g, 0.16 mol) yielded **5d** (33 g, 73%) which was recrystallized from ethyl acetate–petroleum ether to give a pure compound, mp 183—184 °C. Found: C, 59.69; H, 4.54; Cl, 12.71%. Calcd for $C_{14}H_{13}ClO_4$: C, 59.90; H, 4.66; Cl, 12.63%.

*1-(*m-*Substituted benzyl) cyclopentane-1,2-dicarboxylic Acid (**6a**, **6b**, and **6d**).* *(a) 1-*m-*Methoxybenzylcyclopentane-1,2-dicarboxylic Acid (**6a**):* A mixture of 9.0 g (0.033 mol) of **5a** suspended in 500 ml of ethyl acetate and 100 mg of Adams-Pt catalyst was stirred in a hydrogen atmosphere at room temperature; 750 ml (theoretically 728 ml) of hydrogen was absorbed. After the catalyst was filtered out, the solvent was removed under reduced pressure. Saturated dicarboxylic acid (**6a**) was obtained quantitatively and used without further purification for the subsequent dehydration.

*(b) 1-*m-*Methylbenzylcyclopentane-1,2-dicarboxylic Acid (**6b**):* Hydrogenation of **5b** (20 g, 0.077 mol) yielded **6b**.

*(d) 1-*m-*Chlorobenzylcyclopentane-1,2-dicarboxylic Acid (**6d**):* Hydrogenation of **5d** (20 g, 0.071 mol) yielded **6d**.

*3,4-(4'-Substituted benzo)-5-oxo-bicyclo[4.3.0]non-3-ene-1-carboxylic Acid (**7a**, **7b**, and **7d**).* *(a) 3,4-(4'-Methoxybenzo)-5-oxo-bicyclo[4.3.0]non-3-ene-1-carboxylic Acid (**7a**):* A solution of **6a** (9.0 g, 0.033 mol) in a mixture of 80 ml of concd sulfuric acid and 20 ml of water was stirred for 24 h at room temperature. From the reaction mixture, **7a** (5.8 g, mp 146—147 °C) was obtained by the usual work-up in a 67% yield. Found: C, 69.14; H, 6.16%. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20%.

*(b) 3,4-(4'-Methylbenzo)-5-oxo-bicyclo[4.3.0]non-3-ene-1-carboxylic Acid (**7b**):* To a solution of **6b** (20 g, 0.076 mol) in 100

ml of benzene was added 100 ml of concentrated sulfuric acid. The mixture was stirred at room temperature for 24 h. By the usual procedure, **7b** (9.0 g, mp 123—124 °C) was obtained in a 48% yield. Found: C, 73.65; H, 6.61%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(d) 3,4-(4'-Chlorobenzo)-5-oxo-bicyclo[4.3.0]non-3-ene-1-carboxylic Acid (7d): By a method similar to that used in the preparation of **7b**, **7d** (mp 182—184 °C, 12.4 g) was obtained from **5d** (20 g, 0.071 mol) in a 66% yield Found: C, 63.52; H, 4.80; Cl, 13.59%. Calcd for $C_{14}H_{13}O_3Cl$: C, 63.52; H, 4.95; Cl, 13.39%.

3,4-(4'-Substituted benzo)-1-hydroxymethyl-5-hydroxybicyclo-[4.3.0]non-3-ene (9a, 9b, and 9d). (a) 3,4-(4'-Methoxybenzo)-1-hydroxymethyl-5-hydrobicyclo [4.3.0] non-3-ene (9a): A solution of 9.8 g (0.038 mol) of **7a** in 50 ml of ether was treated with a distilled solution of diazomethane in 350 ml of ether, prepared from 40 g (*ca.* 0.19 mol) of *p*-toluenesulfonylmethylnitrosoamide. The reaction mixture was kept in an ice bath for 5 h, ether was removed under reduced pressure, and the keto ester (**8a**) (mp 88—89 °C, 8.5 g, 81%) was obtained. Found: C, 69.86; H, 6.64%. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%.

A solution of **8a** (6.27 g, 0.023 mol) in 350 ml of ether was gradually added into a mixture of 5.3 g of $LiAlH_4$ and 100 ml of ether with stirring in an ice bath. After the mixture was stirred at room temperature for 24 h, a minimum amount (12 ml) of water was added to the mixture. Repeated extraction with $CHCl_3$ yielded the crude product, which was recrystallized from $CHCl_3$ to give 3.06 g (54%) (mp 156—157 °C) of **9a** and 2.47 g (43%) (mp 130—135 °C) of a mixture consisting of **9a** and its epimer. The minor diol was not oxidized with active MnO_2 in benzene, while under the same conditions **9a** was smoothly oxidized into keto alcohol (**10a**). Elemental Analysis for **9a**, Found: C, 72.65; H, 8.00%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

(b) 3,4-(4'-Methylbenzo)-1-hydroxymethyl-5-hydroxybicyclo [4.3.0] non-3-ene (9b). Esterification of **7b** (12.2 g) with diazomethane yielded keto ester (**8b**) (mp 66—67 °C, 12.0 g). Found: C, 74.20; H, 7.06%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%.

Reduction of **8b** (5.3 g, 0.02 mol) with $LiAlH_4$ (3.8 g) yielded **9b** (2.3 g, 47%), a mixture of **9b** and its epimer (1.4 g, mp 114—118 °C, 29%), and an oily product (0.9 g). **9b** was purified by recrystallization from $CHCl_3$, mp 164—165 °C. The epimer of **9b** was not oxidized with active MnO_2 in benzene as above.

(d) 3,4-(4'-Chlorobenzo)-1-hydroxymethyl-5-hydroxybicyclo [4.3.0] non-3-ene (9d): By a method similar to that used in the preparation of **9a**, **9d** (3.0 g, mp 162—163 °C, 56%) and the mixture of **9d** and its epimer (1.5 g, mp 115—125 °C, 28%) were obtained from **8d** (mp 88—89 °C) prepared by esterification of **7d** (5.6 g, 0.021 mol). Elemental analysis for **8d**, Found: C, 64.44; H, 5.22; Cl, 12.81%. Calcd for $C_{15}H_{15}O_3Cl$: C, 64.64; H, 5.43; Cl, 12.71%. **9d**, Found: C, 66.38; H, 6.66; Cl, 13.96%. Calcd for $C_{15}H_{17}O_2Cl$: C, 66.53; H, 6.78; Cl, 14.02%.

3,4-(4'-Substituted benzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-one (11a, 11b, and 11d). (a) 3,4-(4'-Methoxybenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-one (11a): A mixture of 890 mg (3.58 mmol) of diol (**9a**) (mp 156—157 °C) and 2 g of active MnO_2, crushed immediately before reaction, was suspended in 100 ml of dry benzene. Stirring was continued for 24 hr at room temperature, followed by filtration and then the solvent was removed under reduced pressure. Without further purification 20 ml of dry pyridine and 1.4 g of *p*-toluenesulfonyl chloride were added with cooling in an ice-water bath. Stirring was continued for 15 h at room temperature, then for 3 h under reflux. The reaction mixture was poured onto a mixture of 50 ml of concentrated hydrochloric acid and ice, followed by extraction with ether. The organic layer was washed with 6M-hydrochloric acid and water, and dried over anhydrous sodium sulfate. Removing the solvent, the residue was treated with petroleum ether followed by filtration through neutral alumina. Evaporation of the solvent under reduced pressure gave an oily product. Crystallization and purification gave rise to 602 mg of **11a** (mp 87—88 °C) in a 74% yield based on **9a**. Found: C, 78.75; H, 6.98%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

(b) 3,4-(4'-Methylbenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-one (11b): By a method similar to that used in the preparation of **11a**, **11b** (mp 89—90 °C, 270 mg, 27%) was obtained from **9b** (mp 164—165 °C, 1.1 g, 4.7 mmol). Found: C, 84.81; H, 7.55%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

(d) 3,4-(4'-Chlorobenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-one (11d): Similar oxidation and elimination of **9d** (mp 162—163 °C, 1.73 g, 6.8 mmol) gave rise to **11d** (mp 105—106 °C, 780 mg, 49%). Found: C, 72.10; H, 5.62; Cl, 15.05%. Calcd for $C_{14}H_{13}OCl$: C, 72.26; H, 5.63; Cl, 15.23%.

3,4-(4'-Substituted benzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-ol (12a, 12b, and 12d). (a) 3,4-(4'-Methoxybenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-ol (12a): To a stirred suspension of 130 mg of $LiAlH_4$ in 120 ml of dry ether was added a solution of 560 mg (2.5 mmol) of **11a** in 100 ml of ether. The mixture was stirred for 1 h at 0 °C and for 20 h at room temperature before the excess hydride was carefully decomposed with 0.5 ml of water. The ether layer was decanted and the precipitate was washed several times with ether. The combined organic layer was dried with anhydrous K_2CO_3. The solvent was removed under reduced pressure to yield 550 mg of a colorless solid. Recrystallization from petroleum ether gave a pure product (**12a**) (460 mg, 80%), mp 135—136 °C, and an oily residue (70 mg). It was found from its NMR spectrum that the oily residue consisted of two components **12a** and **13a**. Found: C, 78.44; H, 7.92%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

(b) 3,4-(4'-Methylbenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-ol (12b): Reduction of **11b** (1.06 g, 4.9 mmol) with $LiAlH_4$ (185 mg) yielded **12b** (940 mg, 89%) which was recrystallized from petroleum ether to give a pure product, mp 68—69 °C and an oily residue (50 mg) which consisted of two components, **12b** and **13b**. Found: C, 83.88; H, 8.68%. Calcd for $C_{15}H_{18}O_2$: C, 84.07; H, 8.47%.

(d) 3,4-(4'-Chlorobenzo)-tricyclo [4.3.1.0^{1,6}] dec-3-en-2-ol (12d): Reduction of **11d** (240 mg, 1.0 mmol) with $LiAlH_4$ (200 mg) yielded **12d** (mp 108—109 °C, 200 mg, 85%) and an oily residue (20 mg) which consisted of two components, **12d** and **13d**. Mass: m^+/e 236 (M^+) and 234 ($C_{14}H_{15}OCl$).

p-*Nitrobenzoate (1a, 1b, and 1d)*. The *p*-nitrobenzoate was prepared by allowing 150 mg (0.065 mmol) of **12a** to react with 240 mg (1.3 mmol) of *p*-nitrobenzoyl chloride in 5 ml of dry pyridine at 5 °C for 24 h. The product was extracted with ether and the organic layer was washed with water, 1M-hydrochloric acid, 5% aqueous sodium hydrogen carbonate, and water. The ether layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. A light yellow solid was recrystallized from cyclohexane to give **1a** (84 mg, 34%), mp 120—121 °C. Found: C, 69.69; H, 5.43; N, 3.65%. Calcd for $C_{22}H_{21}NO_5$: C, 69.64; H, 5.58; N, 3.69%. By a similar method **1b** (mp 121—122 °C, 58%) and **1d** (mp 144—145 °C, 60%) were obtained. Elemental analysis for **1b**; Found: C, 72.43; H, 5.73; N, 3.80%. Calcd for $C_{22}H_{21}NO_3$: C, 72.71; H, 5.82; N, 3.85%. For **1d**; Found: C, 66.25; H, 4.63; N, 3.50; Calcd for $C_{21}H_{18}NO_4Cl$: C, 65.71; H, 4.73; N, 3.65.

General Kinetic Procedures. For each run approximately 50 mg (*ca.* 0.15 mmol) of *p*-nitrobenzoate (**1a**—**d**) was weighed into a 50 ml volumetric flask and dissolved in 80% aqueous acetone (*ca.* 3×10^{-3} M). The rate at each temperature (to an accuracy of $\pm$0.03 °C at 25 and 45 °C, and $\pm$0.1 °C at 0 °C) was measured by seven quenching 5.00 ml aliquotes in 20 ml of dry acetone and immediately titrated with a standard aqueous sodium hydroxide solution (*ca.* 0.01M) to a blue end point, using 2 drops of a 1% methanol sodium of Bromothymol Blue as an indicator. The reported values are the average of two runs (Table 2). In all cases infinite titers were measured after *ca.* 10 half-lives and 97 to 102% of the *p*-nitrobenzoic acid was removed. In the case of **1a** (X=MeO), the rate was so fast even at 25 °C that the rate constant was determined by three quenching titers at this temperature.

Preparative Solvolysis of p-*Nitrobenzoate (1a, 1b, 1c, and 1d). General Method.* A solution of 0.26 mmol of **1c** and 0.5 ml (*ca.* 2.5 mmol) of 2,6-lutidine in 100 ml of 80% acetone–water was heated at 40 °C for *ca.* 40 half-lives. The solution was concentrated under reduced pressure, 50 ml of water was added and the resulting suspension was extracted with ether. The combined ether extracts were washed with water and dried over anhydrous K_2CO_3. Removing the solvent under reduced pressure gave 50 mg of a light yellow oil. Starting from **1c**, the NMR spectrum of the product thus obtained in $CDCl_3$ was essentially identical with the spectrum of a mixture of **12c**, **13c**, and **14c** in the ratio cited previously from five independent experiments.[10] On the basis of this result, the solvolysis product was determined to consist of **12**, **13**, and **14** in each substituent series by comparison of the NMR spectrum with that of the **c**-series (X=H). Then, product distributions were determined by the average ratio of NMR integral values of the vinyl proton signal for **14**, to those of the α-proton signals for **12** and **13** in five runs. The chemical shifts (δ) of the α-proton and vinyl proton signals of the products and the product distributions are

Table 5. IR and ^{1}H-NMR spectral data of **1a—d** to **12a—d**

Compound	IR[a] (cm^{-1})	^{1}H-NMR δ (ppm) in $CDCl_3$			
		Aromatic	Benzylic	Cyclopentyl	Others
1a	1710 (CO_2R), 1600 1520 (NO_2), 1340 (NO_2)	8.33 (s, 4H), 7.10 (d, J=9.0 Hz, 1H), 6.77 (dd, J=9.0, 2.0 Hz, 1H), 6.67 (d, 2.0 Hz, 1H)	3.26, 2.90 (ABq, J=15.0 Hz, 2H)	2.1—1.2 (m, 6H)	6.60 (s, 1H, α-hydrogen), 3.80 (s, 3H, methyl), 0.70, 0.53 (ABq, J=6.0 Hz, 2H, cyclopropyl)
1b	1715 (CO_2R), 1600 1515 (NO_2), 1345 (NO_2)	8.28 (s, 4H), 6.98 (s, 3H)	3.22, 2.90 (ABq, J=15.0 Hz, 2H)	2.1—1.2 (m, 6H)	6.54 (s, 1H, α-hydrogen), 2.31 (s, 3H, methyl), 0.66, 0.52 (ABq, J=6.0 Hz, 2H, cyclopropyl)
1c	1715 (CO_2R), 1605 1530 (NO_2), 1345 (NO_2)	8.37 (s, 4H), 7.23 (s, 4H)	3.22, 2.90 (ABq, J=15.0 Hz, 2H)	2.1—1.2 (m, 6H)	6.69 (s, 1H, α-hydrogen), 0.66, 0.52 (ABq, J=6.0 Hz, 2H, cyclopropyl)
1d	1715 (CO_2R), 1605 1510 (NO_2), 1345 (NO_2)	8.36 (s, 4H), 7.16(s, 3H)	3.29, 2.93 (ABq, J=16.0 Hz, 2H)	2.1—1.4 (m, 6H)	6.60 (s, 1H, α-hydrogen), 0.64, 0.50 (ABq, J=6.0 Hz, 2H, cyclopropyl)
2a	1750, 1730 (CO) 1600	7.20—6.90 (m, 1H) 6.65—6.55 (m, 3H)	3.00 (s, 2H)	2.5—1.4 (m, 6H)	3.68 (s, 3H, methyl), 3.70 (s, 3H, methyl)
2b	1750, 1730 (CO), 1610	7.18—6.90 (m, 4H)	3.10 (s, 2H)	2.5—1.4 (m, 6H)	3.70 (s, 3H, methyl), 2.28 (s, 3H, methyl)
2c	1730 (CO), 1600	7.20 (s, 5H)	3.10 (s, 2H)	2.5—1.4 (m, 6H)	3.70 (s, 3H, methyl)
2d	1750, 1730 (CO), 1600	7.3—7.0 (m, 4H)	3.25, 2.90 (ABq, J=13.5 Hz, 2H)	2.5—1.4 (m, 6H)	3.70 (s, 3H, methyl)
3a	3380 (OH), 2250 (CN), 1740 (CO_2Me), 1600	7.32—7.06 (m, 1H), 6.90—6.60 (m, 3H)	3.38, 2.63 (ABq, J=13.5 Hz, 2H)	2.5—1.5 (m, 7H, contained OH)	3.75 (s, 3H, methyl), 3.66 (s, 3H, methyl)
3b	3340 (OH), 2250 (CN), 1730 (CO_2Me)	7.30—6.80 (m, 4H)	3.37, 2.62 (ABq, J=13.5 Hz, 2H)	2.5—1.5 (m, 7H, contained OH)	3.66 (s, 3H, methyl), 2.31 (s, 3H, methyl)
3c	3380 (OH), 2250 (CN), 1735 (CO_2Me),	7.42—7.02 (m, 5H)	3.30, 2.70 (ABq, J=13.5 Hz, 2H)	2.4—1.7 (m, 7H, contained OH)	3.70 (s, 3H, methyl)
3d	3340 (OH), 2250 (CN), 1740, 1600	7.26—6.95 (m, 4H)	3.38, 2.64 (ABq, J=13.5 Hz, 2H)	2.5—1.7 (m, 7H, contained OH)	3.68 (s, 3H, methyl)
4a	2210 (CN), 1720 (CO_2Me), 1600	7.25—6.97 (m, 1H) 6.75—6.55 (m, 3H)	3.20, 2.95 (ABq, J=13.0 Hz, 2H)	2.70—2.0(m, 4H)	6.63(t, J=1.5 Hz, 1H, vinyl), 3.76 (s, 3H, methyl), 3.70 (s, 3H, methyl)
4b	2210 (CN), 1730 (CO_2Me), 1610	7.24—6.99 (m, 4H)	3.25, 2.95 (ABq, J=13.0 Hz, 2H)	2.8—1.9 (m, 4H)	6.64 (t, J=1.5 Hz, 1H, vinyl), 3.76(s, 3H, methyl), 2.31 (s, 3H, methyl)

Table 5. (continued)

Compound	IR[a] (cm^{-1})	^{1}H-NMR δ (ppm) in $CDCl_3$			
		Aromatic	Benzylic	Cyclopentyl	Others
4c	2230 (CN), 1730 (CO_2Me)	7.28 (s, 5H)	3.25, 2.95 (ABq, J=13.5 Hz, 2H)	2.6—1.85(m, 4H)	6.69 (t, J=2.5 Hz, 1H, vinyl), 3.78 (s, 3H, methyl)
4d	2220 (CN), 1735 (CO_2Me), 1600	7.26—7.05 (m, 4H)	3.29, 2.99 (ABq, J=13.0 Hz, 2H)	2.7—1.95(m, 4H)	6.69 (t, J=1.5 Hz, 1H, vinyl), 3.77 (s, 3H, methyl)
5a	2600, 1690(CO_2H), 1630				
5b	2600, 1690(CO_2H), 1630				
5c	2600, 1690(CO_2H), 1620				
5d	2600, 1700(CO_2H), 1650, 1600				
6a	1700(CO_2H), 1600	7.25—7.00 (m, 1H), 6.77—6.65 (m, 3H)	3.31, 2.74 (ABq, J=13.5 Hz, 2H)	2.4—1.6 (m, 6H)	10.90 (s, 2H, carboxyl), 3.70 (s, 3H, methyl), 3.31 (m, 1H, methine)
6b	1700(CO_2H), 1600	7.00 (s, 4H)	3.30, 2.73 (ABq, J=13.5 Hz, 2H)	2.0—1.7(m, 6H)	11.60 (s, 2H, carboxyl), 3.30 (m, 1H, methine), 2.25 (s, 3H, methyl)
6c	1685 (CO_2H)	7.20 (s, 5H)	3.34, 2.78 (ABq, J=13.5 Hz, 2H)	2.2—1.7(m, 6H)	11.35 (s, 2H, carboxyl), 3.32 (m, 1H, methine)
6d	1700(CO_2H), 1600	7.16 (s, 4H)	3.36, 2.73 (ABq, J=13.5 Hz, 2H)	2.2—1.6(m, 6H)	11.96 (s, 2H, carboxyl), 3.33 (m, 1H, methine)
7a	1700 (CO_2H), 1675 (CO)	7.95 (d, J=9.0 Hz, 1H), 6.95 (dd, J=9.0, 1.5 Hz, 1H), 6.69 (d, 1.5 Hz, 1H)	3.28, 2.90 (ABq, J=18.0 Hz, 2H)	2.5—1.5(m, 6H)	9.21 (s, 1H, carboxyl), 3.80 (s, 3H, methyl), 3.30 (m, 1H, methine)
7b	1690 (CO_2H, CO)	7.86 (d, J=9.0 Hz, 1H), 7.08 (dd, J=9.0, 1.5 Hz), 7.00 (d, J=1.5 Hz)	3.28, 2.90 (ABq, J=18.0 Hz, 2H)	2.5—1.5(m, 6H)	9.95 (s, 1H, carboxyl), 3.30 (m, 1H,methine), 2.35 (s, 3H, methyl)
7c	1680 (CO_2H), 1670 (CO)	8.20—7.7 (m, 1H), 7.65—7.00 (m, 3H)	3.31, 2.96 (ABq, J=18.0 Hz, 2H)	2.5—1.5(m, 6H)	11.08 (s, 1H, carboxyl), 3.35 (m, 1H, methine)
7d	1700 (CO_2H, CO), 1600	7.93 (d, J=9.0 Hz, 1H), 7.30 (dd, J=9.0, 1.5 Hz, 1H), 7.22 (d, J=1.5 Hz, 1H)	3.30, 2.93 (ABq, J=18.0 Hz, 2H)	2.5—1.5(m, 6H)	10.20 (s, 1H, carboxyl), 3.33 (m, 1H, methine)
8a	1725 (CO_2Me), 1665 (CO), 1595	7.97 (d, J=9.0 Hz, 1H), 6.81 (dd, J=9.0, 1.5 Hz, 1H), 6.72 (d, J=1.5 Hz, 1H)	3.28, 2.91 (ABq, J=17.0 Hz, 2H)	2.4—1.6(m, 6H)	3.81 (s, 3H, methyl), 3.59 (s, 3H, methyl), 3.30 (m, 1H, methine)
8b	1730 (CO_2Me), 1675 (CO), 1610	7.92 (d, J=9.0 Hz, 1H), 7.14 (dd, J=9.0, 1.5 Hz, 1H), 7.06 (d, J=1.5 Hz, 1H)	3.33, 2.96 (ABq, J=17.0 Hz, 2H)	2.4—1.6(m, 6H)	3.61 (s, 3H, methyl), 3.40 (m, 1H, methine)
8c	1730 (CO_2Me) 1670 (CO)	8.00 (dd, J=8.0, 1.5 Hz, 1H), 7.65—7.05 (m, 3H)	3.37, 2.97 (ABq, J=16.0 Hz, 2H)	2.3—1.7(m, 6H)	3.60 (s, 3H, methyl), 3.40 (m, 1H, methine)
8d	1725 (CO_2Me), 1680(CO), 1595	7.93 (d, J=9.0 Hz, 1H), 7.30 (dd, J=9.0, 1.5 Hz, 1H), 7.23 (d, J=1.5 Hz, 1H)	3.33, 2.93 (ABq, J=17.0 Hz, 2H)	2.4—1.6(m, 6H)	3.60 (s, 3H, methyl) 3.36 (m, 1H, methine)
9a	3300 (OH), 1620, 1595				
9b	3250 (OH), 1620				
9c	3300 (OH)				

Table 5. (continued)

Compound	IR[a] (cm^{-1})	^{1}H-NMR δ (ppm) in $CDCl_3$			
		Aromatic	Benzylic	Cyclopentyl	Others
9d	3300 (OH), 1625				
10a	3400 (OH), 1660 (CO), 1595	7.94(d, J=9.0Hz, 1H), 6.79(dd, J=9.0, 2.0 Hz, 1H), 6.70 (d, J=2.0 Hz, 1H)	3.59, 3.40 (ABq, J=12.0 Hz, 2H)	2.3—1.5(m, 6H)	3.82 (s, 3H, methyl), 2.89 (s, 2H, oxmethyl), 2.75 (m, 1H, methine), 2.78 (s, 1H, hydroxyl)
10b	3400 (OH), 1660 (CO), 1605	7.86 (d, J=8.0 Hz, 1H), 7.10(dd, J=8.0, 1.5 Hz, 1H), 7.04(d, J=1.5 Hz, 1H)	3.16, 3.41 (ABq, J=11.0 Hz, 2H)	2.2—1.6(m, 6H)	2.90 (s, 2H, oxymethyl), 2.47 (s, 3H, methyl), 2.65 (m, 1H, methine), 1.90 (s, 1H, hydroxyl)
10c	3430 (OH), 1670 (CO)	8.06 7.80 (m, 1H) 7.70 7.05 (m, 3H)	3.52 (s, 2H)	2.5—1.6(m, 7H contained OH)	2.95 (s, 2H, oxmethyl), 2.70 (m, 1H, methine)
10d	3450 (OH), 1660 (CO), 1595	7.89 (d, J=9.0 Hz, 1H), 7.26(dd, J=9.0, 1.0 Hz, 1H), 7.20 (d, J=1.0 Hz, 1H)	3.59, 3.40 (ABq, J=12.0 Hz, 2H)	2.3—1.6(m, 7H contained OH)	2.93 (s, 2H, oxymethyl) 2.75—2.60(m, 1H, methine)
11a	1645 (CO)	7.88 (d, J=8.2 Hz, 1H), 6.81 (dd, J=8.2, 2.2 Hz, 1H), 6.68 (d, J=2.2 Hz, 1H)	3.37, 3.00 (ABq, J=18.0 Hz, 2H)	2.4—1.5(m, 6H)	3.80 (s, 3H, methyl), 1.23, 1.00 (ABq, J=6.0 Hz, 2H cyclopropyl)
11b	1650 (CO), 1605	7.80 (d, J=8.0 Hz, 1H), 7.10(dd, J=8.0, 2.0 Hz, 1H), 7.00 (d, J=2.0Hz, 1H)	3.36, 3.00 (ABq, J=17.0 Hz, 2H)	2.3—1.5(m, 6H)	2.33 (s, 3H, methyl), 1.22, 1.00 (ABq, J=6.0 Hz, 2H, cyclopropyl)
11c	1665 (CO), 1600	8.00—7.60 (m, 1H) 7.55—6.96 (m, 3H)	3.39, 3.02 (ABq, J=18.9 Hz, 2H)	2.4—1.4(m, 6H)	1.24, 1.05 (ABq, J=6.0 Hz, 2H, cyclopropyl)
11d	1655 (CO), 1595	7.80 (d, J=8.0 Hz, 1H), 7.23 (dd, J=8.0, 1.5 Hz, 1H), 7.15 (d, J=1.5 Hz, 1H)	3.35, 2.98 (ABq, J=16.5 Hz, 2H)	2.3—1.5(m, 6H)	1.25, 1.03 (ABq, J=6.0 Hz, 2H, cyclopropyl)
12a	3350 (OH), 1610	7.56 (d, J=9.0 Hz, 1H), 6.76 (dd, J=9.0, 2.0 Hz, 1H), 6.61 (d, J=2.0 Hz, 1H)	3.16, 2.82 (ABq, J=16.0 Hz, 2H)	2.4—1.4(m, 7H contained OH)	4.84 (s, 1H, α-hydrogen), 3.80 (s, 3H, methyl), 0.36 (s, 2H, cyclopropyl)
12b	3350 (OH), 1610	7.56 (d, J=9.0 Hz, 1H), 7.03 (dd, J=9.0, 2.0 Hz, 1H), 6.90 (d, J=2.0 Hz, 1H)	3.16, 2.82 (ABq, J=16.0 Hz, 2H)	2.4—1.2(m, 7H contained OH)	4.83 (s, 1H, α-hydrogen), 2.30 (s, 3H, methyl). 0.36 (s, 2H, cyclopropyl)
12c	3350 (OH)	7.70—7.40 (m, 1H) 7.30—6.90 (m, 3H)	3.15, 2.79 (ABq, J=16.0 Hz, 2H)	2.5—1.3(m, 7H contained OH)	4.83 (s, 1H, α-hydrogen), 0.36 (s, 2H, cyclopropyl)
12d	3250 (OH), 1600	7.60 (d, J=9.0, 1H), 7.2—7.0 (m, 2H)	3.14, 2.77 (ABq, J=16.0 Hz, 2H)	2.4—1.4(m, 7H contained OH)	4.82 (s, 1H, α-hydrogen), 0.35 (s, 2H, cyclopropyl)

a) Infrared spectra of **2a—d** and **4a—d** were recorded in neat and those of the other compounds in Nujol mulls.

summarized in Table 3.

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