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Methylene Analogs of Cyclobutenedione. IV.[1] The Reaction of 3,4-Bis(diphenylmethylene)cyclobutanedione Monoacetal and Its Derivatives with Methanolic Potassium Hydroxide

Fumio TODA and Nobuhiro OOI
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama

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The reaction of 2,2-dimethoxy-3,4-bis(diphenylmethylene)cyclobutanone (II), 2,2-dimethoxy-3,4-bis(diphenylmethylene)cyclobutanol (III), 2-hydroxy-3,4-bis(diphenylmethylene)cyclobutanone (IV), and 2-methoxy-3,4-bis(diphenylmethylene)cyclobutanol (VIII) with methanolic potassium hydroxide was studied. The three methoxy compounds, II, III, and VIII, afforded the ring-opened products, methyl 4,4-dimethoxy-2-diphenylmethylene-3-diphenylmethylbut-3-enate (X), 4,4-dimethoxy-2-diphenylmethylene-3-diphenylmethylbut-3-enal (XIII), and 4-methoxy-2-diphenylmethylene-3-diphenylmethylbut-3-enal (XVI) respectively. However, the ketoalcohol IV afforded the enolizable cyclobutenedione, 3,4-bis(diphenylmethyl)cyclobutenedione (XXI).

In a previous paper of this series,[1] we have reported the reaction of 2-bromo- (Ia) and 2,2-dibromo-3,4-bis(diphenylmethylene)cyclobutanone (Ib) with alcoholic potassium hydroxide to afford ring-opened products. In the reaction, it has been established that the base attacks the carbonyl initially. In order to certify the generality of the reaction mode, we have studied the reactions of II, III, IV, and VIII with methanolic potassium hydroxide.

Preparation of Compounds II, III, IV, and VIII. The ketoketal II was prepared in a 73% yield according to a previously-reported method,[2] the heating of Ib with methanol. The compound was also prepared in a 91% yield by the heating of a solution of 3,4-bis(diphenylmethylene)cyclobutanedione (VI)[2] in methanol containing a catalytic amount of hydrogen chloride.

The reduction of II in methanol with sodium borohydride afforded the corresponding alcohol III in almost a quantitative yield. The structure of III was identified by means of the spectral data[3] described in the Experimental section. Particularly, the elec-

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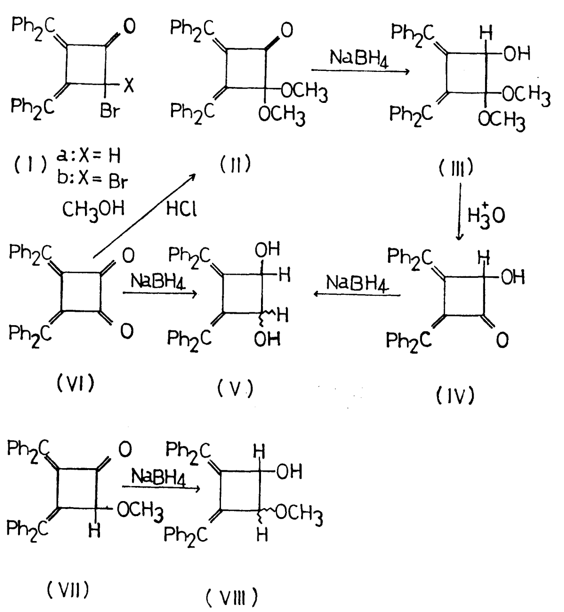
[1] Part III, F. Toda and Y. Takehira, This Bulletin, **45**, 1816 (1972).

[2] F. Toda and K. Akagi, *Tetrahedron*, **27**, 2801 (1971).



Scheme 1.

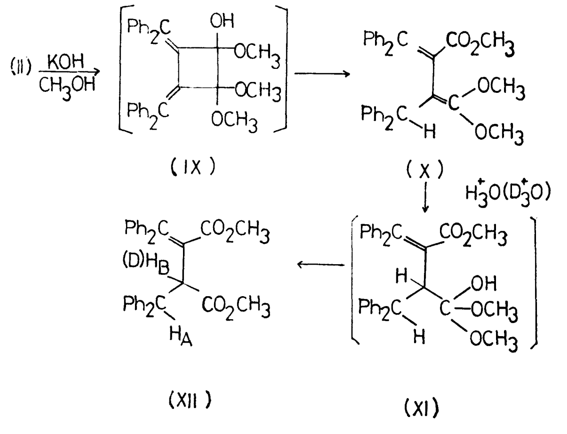
tronic absorption band of III, 365 nm (ε, 16800), was comparable to those of various 1,2-bis(diphenylmethylene)cyclobutane derivatives, 357—400 nm (ε, 15000—20000).[2,4]

The acid-catalyzed hydrolysis of III afforded the keto alcohol IV in a quantitative yield. The structure of IV was determined by means of the spectral data (Experimental section).

The structure of IV was further confirmed by the sodium borohydride reduction to the corresponding diol V, the spectral data of which were identical with those recorded for the diol[2,5] prepared by the sodium borohydride reduction of VI. Of the three compounds prepared, II, III, and IV, III differs in stability from the other two. In an atmosphere, III decomposed gradually and was converted finally into IV.

Monomethoxycyclobutanol VIII was obtained in a 46% yield by the sodium borohydride reduction of VII, which had been prepared by the reaction of Ia with methanol in the presence of silver perchlorate according to a previously-reported procedure.[2] The structure of VIII was identified by means of the spectral data (Experimental section), even though the configurational relationship between hydroxy and methoxy was not clear.

The Reaction with Methanolic Potassium Hydroxide. The heating of a solution of II and potassium hydroxide in methanol under reflux for 17 hr afforded X in a 72% yield. The structure of X was determined by means of the spectral data (Experimental section). In the NMR spectrum, X showed two methoxy methyl signals at 6.58 and 7.24 τ. The nonequivalence of the two methoxy methyls agrees with the structure bearing a *gem*-dimethoxy ethylene moiety. The structure of X was further identified by an acid-catalyzed hydrolysis, which afforded dimethyl 2-diphenylmethyl-3-diphenylmethylenesuccinate (XII), probably *via* the intermediate XI (Scheme 2). The structure of XII was identified by means of the spectral data described in the Experimental section. The assignment of the two AB-type doublets, 4.90 and 5.40 τ, was performed with using the monodeutero compound XII-*d*, prepared by the reaction of X with DCl in D_2O. Since XII-*d* showed a singlet at 4.92 τ, the doublet at the lower field (4.90 τ) can be assigned to the benzylic methine proton, H_A.



Scheme 2.

The reaction of II with methanolic potassium hydroxide to afford X can be interpreted by assuming the trimethoxy alcohol IX, as an intermediate. Therefore, the alcohol IX, initially produced by the action of methoxy anion on the carbonyl of II can be led to X by ketonization, accompanied by ring-opened, as is shown in Scheme 2. If the assumption is correct, the alcohols III and VIII would react with methanolic potassium hydroxide in the same fashion as that of II.

The reaction of III with methanolic potassium hydroxide under the same conditions as those employed for II was completed in 1 hr and afforded XIII in a quantitative yield. The structure of XIII was identified by means of the spectral data. IR, 2720 (CHO), 1665—1650 (C=O and C=C) and 1240 and 1230 cm^{-1} (C=C–O); UV, 291 (8700) and 356 nm (ε, 3800); NMR, 0.66 (s, CHO, 1H), 2.5—3.5 (m, C_6H_5, 20H), 5.51 (s, CH, 1H), 6.51 (s, OCH_3, 3H) and 7.22 τ (s, OCH_3, 3H). The UV spectrum of XIII was comparable to that of X. Since the two absorption bands of $\nu_{C=O}$ and $\nu_{C=C}$ overlapped and appeared at 1665—1650 cm^{-1} as a broad band, it was impossible to assign each band. The presence of a methoxy-substituted ethylene was certified for the 4,4-dimethoxy-3-diphenylmethyl-2-diphenylmethylenebut-3-enol (XV) obtained quantitatively by the sodium borohydride reduction of XIII. The alcohol XV showed a strong band at 1665 cm^{-1} which was assignable to the methoxy-substituted ethylene.

Further structural proof for XIII was obtained by means of its acid-catalyzed reaction. The treatment of XIII with hydrochloric acid under the same condi-

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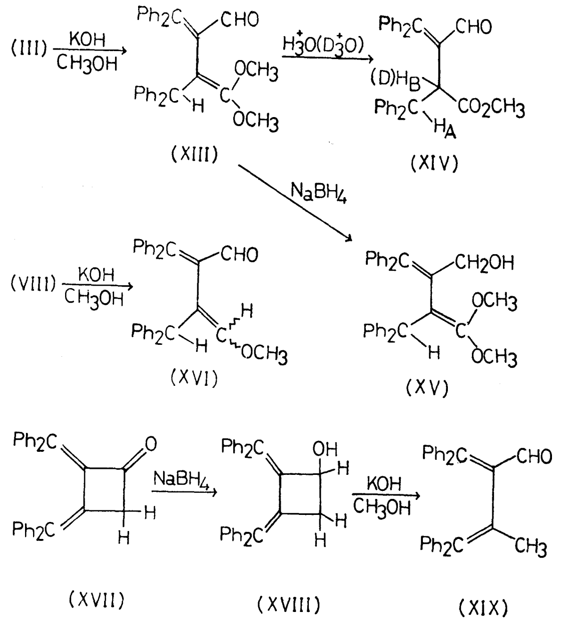
[3] All the IR, UV, and NMR spectra were recorded in Nujol mull, ethanol, and $CDCl_3$ respectively.

[4] F. Toda, K. Kumada, N. Ishiguro, and K. Akagi, This Bulletin, **43**, 3535 (1970).

[5] F. Toda, H. Ishihara, and K. Akagi, *Tetrahedron Lett.*, **1969**, 2531.



Scheme 3.

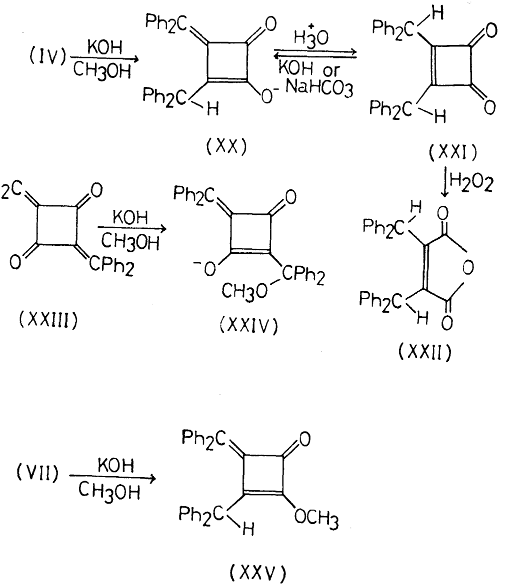
tions as those employed for X afforded methyl 2-diphenylmethyl-3-formyl-4,4-diphenylbut-3-enate (XIV) quantitatively. The structure of XIV was determined by means of the spectral data described in the Experimental section. The assignment of the two AB-type doublets of XIV, 4.88 and 5.34 τ, was performed again on the monodeutero derivative, XIV-*d*, prepared by the reaction of XIII with DCl in D_2O. Since XIV-*d* showed a singlet at 4.89 τ, but no other methine proton signal, the signal at 4.88 τ of XIII can be assigned to the benzylic methine proton, H_A.

The same reaction mode as that of II and III was observed in the case of VIII. The heating of VIII with methanolic potassium hydroxide under reflux for 5 hr afforded 4-methoxy-3-diphenylmethyl-2-diphenylmethylenebut-3-enal (XVI) in a 56% yield. The structure of XVI was identified by means of the spectral data. IR, 2720 (CHO), 1670 (C=O) and 1640 cm^{-1} (C=C); UV, 248 (16200), 299 (8600) and 370 sh nm (ε, 3600); NMR, 0.76 (s, CHO, 1H), 2.81 (m, C_6H_5, 18H), 3.34 (m, C_6H_5, 2H), 4.52 (d, $J=0.7$ Hz, =CH, 1H), 5.41 (d, $J=0.7$ Hz, CH, 1H) and 6.48 τ (s, CH_3, 3H). The NMR spectral data show the presence of a coupling between the methine proton and the vinyl proton. Since the long-range coupling across one double and three single bonds is well established as an allylic coupling,[6] the NMR spectrum of XVI can be well interpreted by its structure. However, the geometry around the double bond bearing the methoxy group was not determined.

A comparison of the three reactions of II, III, and VIII with methanolic potassium hydroxide makes it clear that the ketone II reacts more slowly than do the alcohols III and VIII. However, it is not clear which, the addition of methanol to the carbonyl of II or the ring-opening of IX, is more retarded.

All the three products, X, XIII, and XVI, have a vinylether structure. It is reasonable to consider that the double bonds of those products are stabilized by one or two methoxy groups, because the reaction of XVIII with methanolic potassium hydroxide afforded 2,3-bis(diphenylmethylene)butan-1-al (XIX). The reaction of XVIII prepared by the sodium borohydride reduction of 2,3-bis(diphenylmethylene)cyclobutanone (XVII) according to a reported method,[2] with methanolic potassium hydroxide under the same conditions as those employed for VIII, was finished within 10 min and afforded XIX in an 80% yield. The structure of XIX was identified by means of the spectral data (Experimental section).

In order to clarify which, the addition of methanol to the carbonyl of II or the ketonization of IX, occurs more easily, the keto alcohol IV, was reacted with methanolic potassium hydroxide. Contrary to expectations, IV did not give any ring-opened product. Although IV is almost insoluble in methanol, it dissolved in methanolic potassium hydroxide easily. The acidification of the solution afforded 3,4-bis(diphenylmethyl)cyclobutenedione (XXI) in a 62% yield.



Scheme 4.

The UV spectrum of IV (or of XXI) in 5% methanolic potassium hydroxide, 330 nm (ε, 21700), was comparable to that of the enolate anion (XXIV) obtained by dissolving 2,4-bis(diphenylmethylene)cyclobutanedione (XXIII) in 5% methanolic potassium hydroxide, 324 nm (ε, 24600).[7] Therefore, IV and XXI must dissolve in the base in the form of the enolate anion, XX. Since the base-catalyzed rearrangement of VII to 4-diphenylmethylene-3-diphenylmethyl-2-methoxycyclobut-2-enone (XXV) has been reported,[1] the base-catalyzed 1,3-hydrogen shift may be characteristic for a system such as IV or VII.

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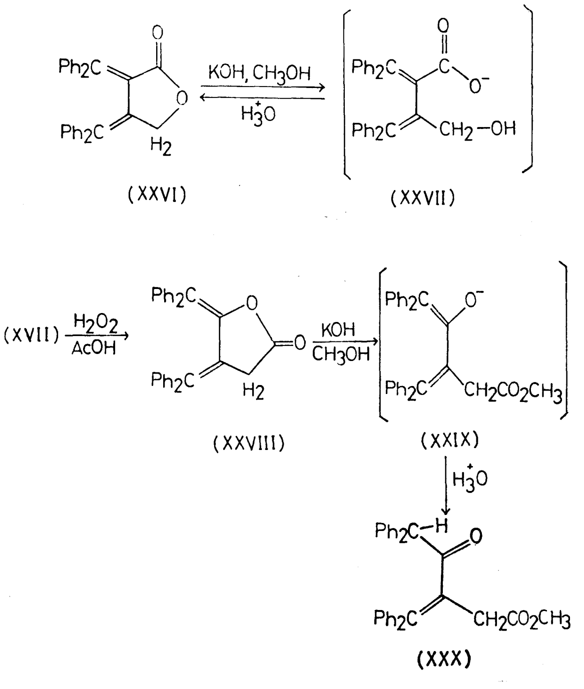
6) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, London (1969), p. 316.

7) G. A. Taylor, *J. Chem. Soc., C*, **1969**, 1755.

All the cyclobutenediones except squaric acid and its derivatives which have been reported to date are sensitive to the base, and all undergo ring-cleavage.[8] The enolization of XXI in the base without ring cleavage differs widely from these facts. The acidity of the benzylic hydrogen of XXI is relatively strong, and XXI dissolves in even methanolic sodium bicarbonate. In connection with the strong acidity[9] of squaric acid, the acidic nature of the hydrogen of XXI is interesting.

Further structural proof for XXI was obtained by oxidation with neutral hydrogen peroxide which afforded bis(diphenylmethyl)maleic anhydride (XXII) in a 24% yield. It is well established that cyclobutenediones undergo a Baeyer-Villiger oxidation with neutral hydrogen peroxide to afford the corresponding maleic anhydrides.[8]



Scheme 5.

Any possibility that the compound derived from IV is a γ-lactone, such as XXVI or XXVIII, is ruled out. 3,4-Bis(diphenylmethylene)-γ-lactone (XXVI) was prepared according to the reported method;[1] it was dissolved in methanolic potassium hydroxide, probably by the formation of a carboxylate anion like XXVII, and XXVI was reformed by acidification. The behavior is similar to that of XXI; however, the spectral data which have been recorded for XXVI differ from those of XXI. 4,5-Bis(diphenylmethylene)-γ-lactone (XXVIII), prepared by the oxidation of XVII according to Corey's procedure,[10] was also dissolved in methanolic potassium hydroxide, probably in the form of an enolate anion like XXIX. However, the ketone XXX was obtained by the acidification of the alkaline solution. Both the spectral data of XXVIII and of XXX are also different from those of XXI (Experimental section).

Experimental[3]

Preparation of III. A suspension of II (5.00 g) in ethanol (100 m*l*) was treated with a large excess of sodium borohydride at 50—60°C for 1 hr. After the reaction mixture had been decomposed with water, the crude product which was separated out was collected by filtration, washed with water, and dried to afford III; 4.71 g (94%). The recrystallization of the product from ethyl acetate gave an analytical pure sample as pale yellow prisms; 4.0 g (80%); mp 131—132°C. IR, 3480 cm^{-1} (OH); UV, 365 nm (ε, 16800); NMR, 2.83 (d, C_6H_5, 10H), 3.18 (d, C_6H_5, 10H), 4.87 (d, J=10 Hz, CH, 1H), 6.53 (s, OCH_3, 3H), 6.83 (s, OCH_3, 3H) and 7.60 τ (d, J=10 Hz, OH, 1H).

Found: C, 83.30; H, 5.97%. Calcd for $C_{32}H_{28}O_3$: C, 83.45; H, 6.13%.

Preparation of IV. To a solution of III (0.60 g) in acetone (10 m*l*), several drops of concentrated hydrochloric acid were added. Crude crystals formed by the addition of water to the reaction mixture were collected by filtration, washed with water, and dried to afford IV; 0.53 g (99%). Recrystallization of the crude crystals from ethyl acetate afforded a pure sample as fine orange needles; 0.425 g (79%); mp 185—186°C. IR, 3420 (OH) and 1775 cm^{-1} (C=O); UV, 271 (15600), 329 (5000) and 422 nm (ε, 9200); NMR, 2.68 (d, C_6H_5, 10H), 3.18 (d, C_6H_5, 10H), 4.44 (s, CH, 1H) and 7.63 τ (s, OH, 1H).

Found: C, 86.74; H, 5.18%. Calcd for $C_{30}H_{22}O_2$; C, 86.93; H, 5.35%.

A suspension of IV (0.25 g) in ethanol (10 m*l*) was treated with a large excess of sodium borohydride at room temperature for 5 min. The crystals formed were collected by filtration, washed with water, and dried to afford V as pale yellow needles; 0.23 g (92%); mp 222—223°C (lit,[2,4] mp 222—223°C). The spectral data were identical with those of an authentic sample prepared according to a previously-reported method.[2,4]

Preparation of VIII. The treatment of VII[2] (0.50 g) in methanol (10 m*l*) with sodium borohydride by the same method as that employed for III afforded VIII as yellow needles; 0.23 g (46%); mp 167—170°C. IR, 3420 cm^{-1} (OH); UV, 365 nm (ε, 17400); NMR, 2.25 (s, C_6H_5, 10H), 3.22 (s, C_6H_5, 10H), 5.18 (d, J=5 Hz, CH, 1H), 5.53 (d, J=5 Hz, CH, 1H), 6.69 (s, CH_3, 3H) and 7.2 τ (broad, OH, 1H).

Found: C, 86.00; H, 5.84%. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09%.

Ring-opening Reaction of II. A solution of II (0.30 g) and a large excess of potassium hydroxide (2.5 g) in THF (15 m*l*) - methanol (35 m*l*) was heated under reflux for 17 hr. After decomposition with water, the crude crystals which separated out were collected by filtration, washed with water, and dried to give X; 0.23 g (74%). Recrystallization from cyclohexane gave pure X as colorless prisms; mp 118—119°C. IR, 1710 (C=O), 1655 (C=C), 1240 (ester) and 1250 cm^{-1} (=C-O-); UV, 238 sh (18300) and 315 nm (ε, 6300); NMR, 2.7—3.2 (m, C_6H_5, 20H), 5.45 (s, CH, 1H), 6.58 (s, OCH_3, 3H), 6.68 (s, CO_2CH_3, 3H) and 7.24 τ (s, OCH_3, 3H).

Found: C, 80.97; H, 6.55%; Calcd for $C_{33}H_{30}O_4$; C, 80.79; H, 6.16%.

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[8] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York and London (1967), pp. 128—156.

[9] S. Cohen, J. R. Lacher, and J. D. Park, *J. Amer. Chem. Soc.*, **81**, 3480 (1959).

[10] E. J. Corey, Z. Arnold, and J. Hutton, *Tetrahedron Lett.*, **1970**, 307.

Acid-catalyzed Hydrolysis of X. A solution of X (0.09 g) in acetone (5 m*l*) containing a catalytic amount of hydrochloric acid was heated at 50—60°C for 5 min. The crude crystals formed by the addition of water were filtered, washed with water, and dried to yield XII; 0.08 g (92%). Recrystallization of the crude crystals from methanol gave pure XII as colorless prisms; mp 164—165°C. IR, 1738 (C=O), 1725 (C=O), 1260 (ester) and 1240 cm^{-1} (ester); UV, 264 nm (ε, 7100); NMR, 2.6—3.3 (m, C_6H_5, 20H), 4.90 (d, J=12 Hz, H_A, 1H), 5.40 (d, J=12 Hz, H_B, 1H), 6.45 (s, CO_2CH_3, 3H) and 6.62 τ (s, CO_2CH_3, 3H).

Found: C, 80.22; H, 5.86%. Calcd for $C_{32}H_{28}O_4$: C, 80.64; H, 5.92%.

Ring-opening Reaction of III. A suspension of III (0.50 g) and potassium hydroxide (0.4 g) in methanol (10 m*l*) was heated under reflux for 1 hr. After decomposition with water, the crude crystals which had formed were filtered, washed with water, and dried to afford XIII; 0.49 g (98%). The recrystallization of the crystals from ethyl acetate yielded pure XIII as yellow prisms; mp 113—114°C.

Found: C, 83.37; H, 5.99%. Calcd for $C_{32}H_{28}O_3$: C, 83.45; H, 6.13%.

The aldehyde XIII (0.09 g) in methanol (5 m*l*) was treated with an excess of sodium borohydride at 50—60°C for 5 min. Crude crystals (0.09 g (100%)) obtained by the decomposition of the reaction mixture were recrystallized from methanol to afford pure XV as colorless prisms; mp 148—148.5°C. IR, 3520 (OH), 1665 (C=C) and 1240 cm^{-1} (=C–O); UV, 237 sh (9500), 271 sh (4200) and 279 sh nm (ε, 3500); NMR, 2.5—3.5 (m, C_6H_5, 20H), 5.45 (s, CH, 1H), 6.05 (d, J=6 Hz, CH_2, 2H), 6.42 (s, OCH_3, 3H), 7.33 (s, OCH_3, 3H) and 8.87 τ (t, J=6 Hz, OH, 1H).

Found: C, 83.06; H, 6.47%. Calcd for $C_{32}H_{30}O_3$: C, 83.01; H, 6.54%.

Acid-catalyzed Hydrolysis of XIII. To a solution of XIII (0.14 g) in acetone, a few drops of concentrated hydrochloric acid were added, and then the mixture was heated at 50—60°C for 5 min. Crystals (0.13 g (96%)) obtained by the addition of water to the reaction mixture were recrystallized from cyclohexane to afford pure XIV as colorless needles; mp 204—205°C. IR, 2720 (CHO), 1745 (CO_2CH_3), 1660 (CHO) and 1240 cm^{-1} (ester); UV, 238 sh (18300) and 315 nm (ε, 6300); NMR, 0.83 (s, CHO, 1H), 2.4—3.7 (m, C_6H_5, 20H), 4.88 (d, J=11 Hz, H_B, 1H), 5.34 (d, J=11 Hz, H_A, 1H) and 6.36 τ (s, CH_3, 3H).

Found: C, 83.71; H, 5.81%. Calcd for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87%.

To a solution of XIII (0.10 g) in THF (5 m*l*), was added a few drops of concentrated deuterochloric acid, and then the mixture was heated at 50—60°C for 5 min. The same treatment of the reaction mixture as above afforded XIV-*d* after recrystallization from cyclohexane; 0.08 g (82%).

Ring-opening Reaction of VIII. A solution of VIII (0.32 g) and potassium hydroxide (0.5 g) in methanol (10 m*l*) was heated under reflux for 5 hr. Crude crystals obtained by the addition of water to the reaction mixture were recrystallized from benzene to afford XVI as yellow prisms; 0.18 g (56%); mp 187°C.

Found: C, 86.25; H, 6.07%. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09%.

Ring-opening Reaction of XVIII. A mixture of XVIII (0.40 g), potassium hydroxide (0.5 g), and methanol (20 m*l*) was heated under reflux for 10 min. Crude crystals obtained by the decomposition of the reaction mixture were recrystallized from petroleum ether (bp 60—70°C) to afford XIX as pale yellow plates; 0.32 g (80%); mp 141—142°C. IR, 2720 (CHO) and 1655 cm^{-1} (C=O); UV, 235 sh (22100), 270 sh (14300) and 305 sh nm (ε, 8600); NMR, 0.55 (s, CHO, 1H), 2.6—3.4 (m, C_6H_5, 20 H) and 7.98 τ (s, CH_3, 3H).

Found: C, 89.60; H, 5.88%. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04%.

Isomerization of IV to XXI. A mixture of IV (1.65 g), potassium hydroxide (1.0 g), and methanol (15 m*l*) was heated under reflux for 5 min to afford a clear solution. The crude crystals obtained by the acidification of the clear solution with hydrochloric acid were recrystallized from methanol to afford XXI as colorless prisms; 1.02 g (62%); mp 130—131°C. IR, 1790 and 1770 (unsplit doublet, C=O) and 1580 cm^{-1} (C=C); UV, 258 sh (9000), 267 sh (7600) and 276 sh nm (ε, 6200); NMR, 2.5—3.0 (m, C_6H_5, 20H) and 4.73 τ (s, CH, 2H).

Found: C, 86.97; H, 5.15%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.

Oxidation of XXI. A mixture of XXI (0.2 g), 30% aqueous hydrogen peroxide (1.5 m*l*), and acetic acid (60 m*l*) was stirred at room temperature for 24 hr. The crude crystals formed by the addition of water to the reaction mixture were recrystallized from methanol to afford XXII as colorless prisms; 0.1 g (48%); mp 171—172°C. IR, 1825 and 1770 (C=O) and 1645 cm^{-1} (C=C); UV, 253 sh (6500), 259 sh (5800) and 282 sh nm (ε, 4000); NMR, 2.85 (d, C_6H_5, 20H) and 4.63 τ (s, CH, 2H).

Found: C, 83.85; H, 5.07%. Calcd for $C_{30}H_{22}O_3$: C, 83.70; H, 5.15%.

The same reaction in acetone for 86 hr afforded XXII in a 24% yield.

Preparation of XXVIII. A mixture of XVII (0.66 g), 30% aqueous hydrogen peroxide (1 m*l*), and acetic acid (60 m*l*) was stirred at 65°C for 10 hr. The crude crystals formed by the addition of water to the reaction mixture were recrystallized from methanol to afford XXVIII as yellow prisms; 0.07 g (10%); mp 216—217°C. IR, 1795 (C=O) and 1620 cm^{-1} (C=C); UV, 251 (29300) and 345 nm (ε, 11100); NMR, 2.6—3.6 (m, C_6H_5, 20H) and 6.53 τ (s, CH_2, 2H).

Found: C, 86.41; H, 5.11%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.

Reaction of XXVIII with Methanolic Potassium Hydroxide. A mixture of XXVIII (0.05 g), potassium hydroxide (0.04 g), and methanol (20 m*l*) was heated under reflux for 15 min. The crude crystals formed by the decomposition of the reaction mixture were collected by filtration and were then recrystallized from methanol to afford XXX as colorless prisms; 0.025 g (46%); mp 106—107°C. IR, 1740 (C=O) and 1670 cm^{-1} (C=O); 290 nm (ε, 4900); NMR, 2.85 (m, C_6H_5, 20H), 5.15 (s, CH, 1H), 6.62 (s, CH_3, 3H) and 6.75 τ (s, CH_2, 2H).

Found: C, 83.72; H, 5.80%. Calcd for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87%.

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