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METHYLENE ANALOGS OF CYCLOBUTADIENEQUINONE—II[1]

PREPARATION AND REACTIONS OF 2-HALO- AND 2,2-DIHALO-3,4-BIS(DIPHENYLMETHYLENE)CYCLOBUTANONE

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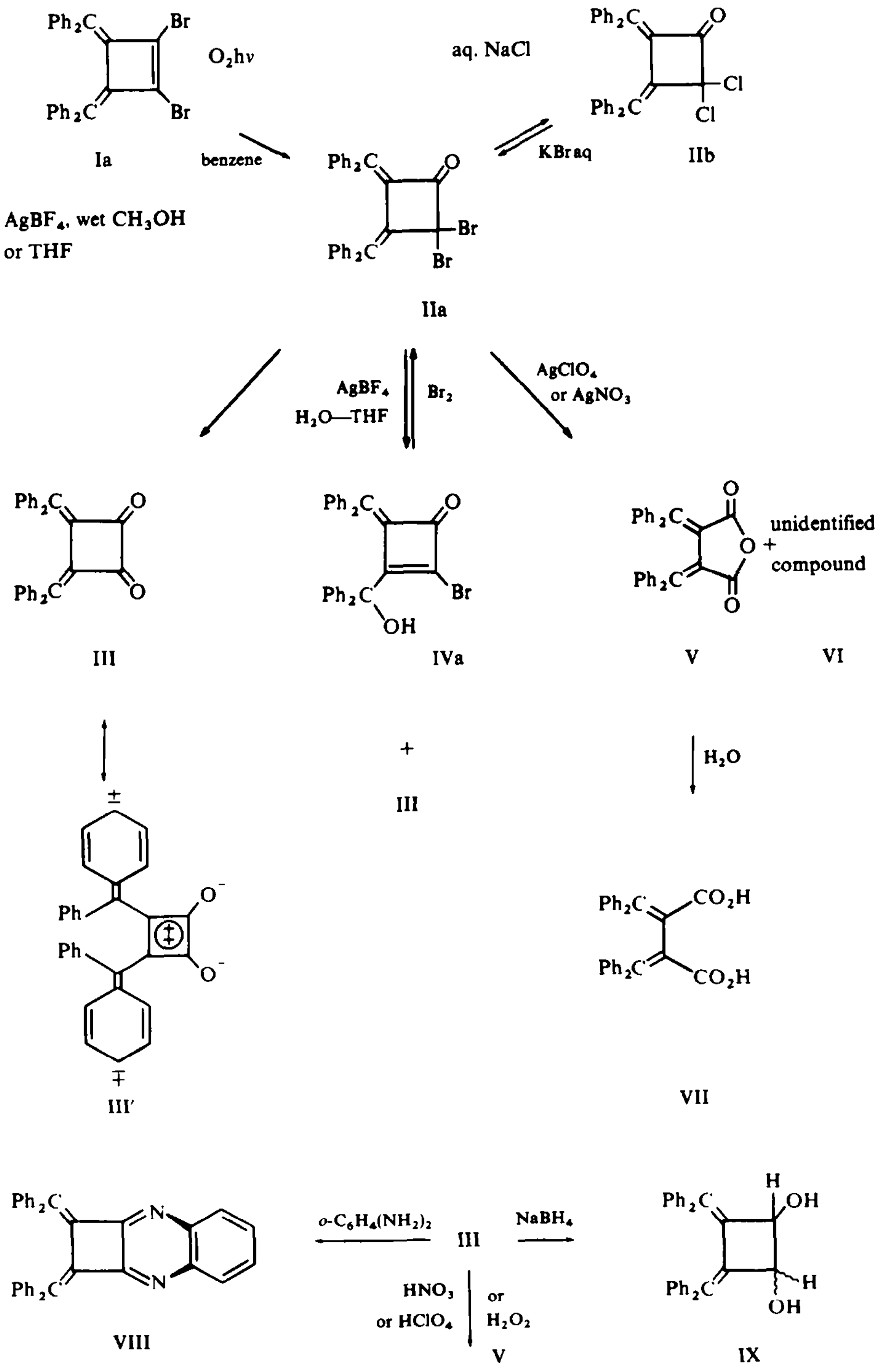
Abstract—The title compounds (II, XVII; dichloro and dibromo derivatives) have been prepared, and some novel reactions of the compounds described.

IN THE study on methylene analogs of cyclobutadienequinone, attention was focussed on the chemistry of the title compounds (II and XVII) which were prepared from 1,2-dihalo-3,4-bis(diphenylmethylene)cyclobutene (I). Of special interest were the reactions of II and XVII with the reagents which abstract the halo anion.

Perchloro-3,4-dimethylenecyclobutanone[2] is the only example of a 2,2-dihalogen-substituted 3,4-dimethylenecyclobutanone. Since 2,2-dihalo-3,4-dimethylenecyclobutanone with no halogen on the methylene carbon was suitable for our purpose, we prepared 2,2-dihalo-3,4-bis(diphenylmethylene)cyclobutanone (II). The photooxidation of Ia[1] afforded IIa as crimson prisms in 50% yield. In a preliminary communication,[3] we assigned the incorrect structure, 3,4-bis(diphenylbromomethyl)cyclobutenedione to this photooxidation product. One reason which has led to the incorrectness is the IR spectral data of IIa showing the strong band of ν C═C at 1540 cm^{-1} in addition to the strong one of ν C═O at 1770 cm^{-1}. Since frequencies[4] of *endo*cyclic C═C bonds fall with increasing ring strain, whereas those of *exco*cyclic bonds rise, we incorrectly assigned the band at 1540 cm^{-1} to the *endo*-double bond. However, it is recognized[4] that ν C═C of the both *endo*- and *exo*-double bonds fall with increasing ring strain, on the basis of new data accumulated on the positions of C═C absorptions in different chemical environments. Therefore, the band at 1540 cm^{-1} of IIa should be assigned to the *exo*-double bond. By the same reason, the medium bands of Ia and Ib, 1510 and 1530 cm^{-1} respectively, may be due to the corresponding *exo*-double bond. The electronic absorption bands of IIa in acetonitrile appear at 260, 270, 346 and 460 nm. The NMR spectrum of IIa shows the presence of only the aromatic protons.

In the behavior of photooxidation, the dichloro-analog of Ia (Ib)[1] was different from Ia, and Ib was not photooxidized into IIb by the same treatment as employed for Ia. The inertness of Ib to photooxidation is in contrast with the reported result[2] that perchlorodimethylenecyclobutene is easily oxidized to perchloro-3,4-dimethylenecyclobutanone. However, IIb was obtained by the heating of a mixture of an acetonitrile solution of IIa and aqueous sodium chloride. The IR spectrum of IIb, 1775 (CO) and 1540 cm^{-1} (C═C), is almost the same as that of IIa except the region


Ia
$O_2h\nu$
benzene
aq. NaCl
KBraq
IIb
IIa
$AgBF_4$, wet CH_3OH or THF
$AgBF_4$
H_2O—THF
Br_2
$AgClO_4$ or $AgNO_3$
III
IVa
+
III
V
unidentified compound
VI
H_2O
III′
VII
VIII
o-$C_6H_4(NH_2)_2$
III
$NaBH_4$
HNO_3 or $HClO_4$
or H_2O_2
V
IX

SCHEME 1

near 850 cm^{-1}. The former shows a strong band at 850 cm^{-1}, whereas the latter shows a medium band at 825 cm^{-1}.

The bromines of the *gem*-dibromoketone IIa are reactive with various reagents which abstract bromo anions, and IIa afforded various products depending on the reagent and the medium employed. For example, when a solution of IIa was treated with an equimolar amount of silver fluoroborate, 3,4-bis(diphenylmethylene)-cyclobutanedione (III) was obtained as green needles or prisms in 90% yield. The structure of III was determined by the spectral data and some chemical reactions. The IR spectrum in Nujol mull showed ν C=O at 1750 cm^{-1} with shoulders at 1770 and 1720 cm^{-1}, ν C=C at 1550 and 1520 cm^{-1}. The NMR spectrum shows only aromatic protons. The electronic spectrum in acetonitrile, 252, 274, 315, 465 sh, 499 and 620 nm, resembles the structure III to which a contribution of the 2π-dication structure (III′) is considerable. The electronic spectrum of III is very similar to that[2] recorded for 3,4-bis(dichloromethylene)cyclobutanedione prepared by the air oxidation of 1-methoxy-2-chloro-3,4-bis(dichloromethylene)cyclobutene. However the physical data of III did not agree with those recorded for a compound obtained by partial ozonolysis of tetrakis(diphenylmethylene)cyclobutane, to which the structure III has been assigned.[5]

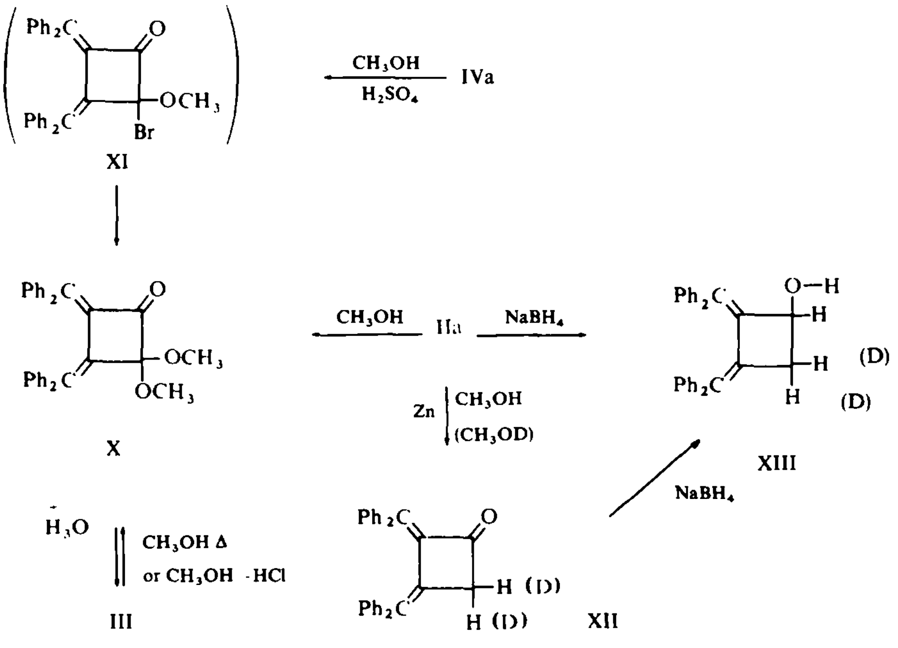
The diketone III formed the quinoxaline derivative (VIII) by the treatment with *o*-phenylenediamine. The sodium borohydride reduction of III afforded the corresponding diol IX quantitatively, even though its geometry has not been established.

The reaction of IIa with silver fluoroborate to afford III can be interpreted by assuming the corresponding *gem*-hydroxybromide which is formed by the substitution of one bromine by hydroxy, as an intermediate. When the reaction was carried out in dried THF, the yield of III was low and a large amount of an oily material was produced. However, when the same reaction was carried out in acetonitrile (or THF) containing 10% water, 2-bromo-3-diphenylhydroxymethyl-4-diphenylmethylene-cyclobut-2-enone (IVa) and III were isolated in 44 and 27% (or 29 and 27%) yields respectively. All the physical data of IVa thus obtained are identical with those of an authentic sample of IVa prepared according to the reaction[6] of 1,1,2,2-tetrabromo-3,4-bis(diphenylmethylene)cyclobutane with silver perchlorate.

The reaction of IVa with bromine afforded IIa immediately. The formation of III can be interpreted by the manner described above. It is interesting that when a large excess of water is present in the medium, the OH attacks the benzyl-carbon but not the ring-carbon by a SN2′ type reaction.

On the other hand, the reaction of IIa with silver perchlorate or nitrate afforded 3,4-bis(diphenylmethylene)succinic anhydride (V) in 85% yield in addition to a small amount of an unidentified compound (VI), m.p. 189–191°. The structure of V was identified by the IR spectrum which shows the two ν C=O bands at 1795 and 1755 cm^{-1}, and ν C=C at 1545 cm^{-1}. The electronic spectral data of V in chloroform, 249, 315 and 424 nm, is also consistent with the structure. The structure of V was finally determined by the comparison of the spectral data of V with an authentic sample prepared by the oxidation of III with hydrogen peroxide. The oxidation of cyclobutadienequinone[7–9] or 3,4-dimethylenecyclobutanedione[2] by hydrogen peroxide to the corresponding anhydride has been reported. Moreover, the alkaline hydrolysis of V afforded the dicarboxylic acid VII. Since the treatment of III with perchloric or nitric acid afforded V easily, the transformation of IIa into V probably proceeds through an oxidation process of III by perchloric or nitric acid, both of which were initially produced by the reaction of IIa with silver perchlorate or nitrate in the presence of water.

The bromines of IIa are also sensitive to alcohol. The heating of a solution of IIa in methanol afforded 2.2-dimethoxy-3.4-bis(diphenylmethylene)cyclobutanone (X) in 73% yield, Scheme 2. The electronic spectrum of X, 275, 336 and 425 nm, was comparable to that of IIa, 274, 342 and 453 nm. The NMR spectrum consisting of two multiplets at 2·65 and 3·10 τ due to 20 aromatic protons and a singlet at 6·55 τ due to 6 Me protons, shows the presence of the two equivalent OMe groups. The IR bands, 1755 (C=O), 1555 (*endo* C=C) and 1100 cm^{-1} (ether), are consistent with the structure X. The ketal structure X was confirmed by acid-catalyzed hydrolysis to give III. The reaction of IIa with methanol may proceed by stepwise substitution of the two bromines by OMe groups. The heating of a methanol solution of III and a catalytic amount of hydrogen chloride also afforded X in almost quantitative yield. In a neutral condition, III reacted with methanol slowly and afforded X. For example, allowing a methanol solution of III to stand at room temperature for 15 days yielded X in 33% yield. The production of X was again encountered in an acid-catalyzed methanolysis of IVa. When a solution of IVa in methanol containing a catalytic amount of conc sulfuric acid was heated,[1] X was obtained in 83% yield. The reaction may proceed *via* the intermediate XI, which was formed by SN2′ type reaction of IVa with methanol. Since, as will be discussed later, the treatment of the 2-hydrogen substituted analog of IVa (XVIII) with methanol-sulfuric acid afforded the hydrogen analog of XI (XIX), it is reasonable to consider XI as an intermediate.



SCHEME 2

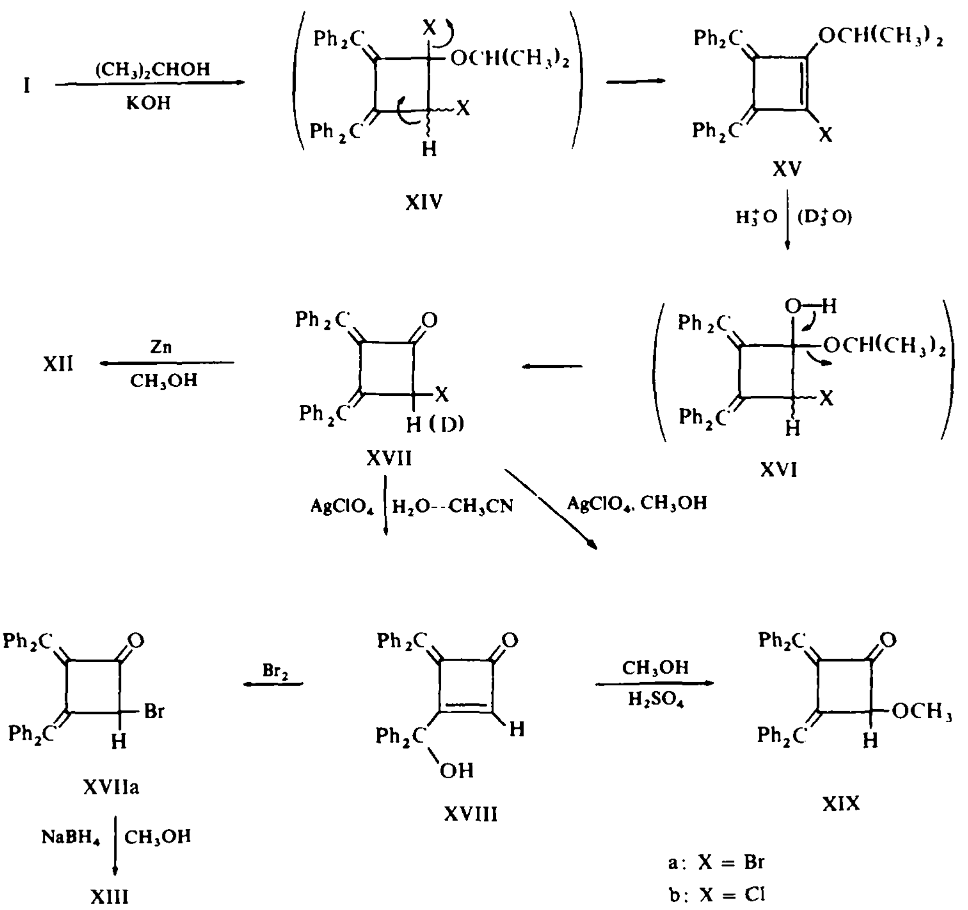
The reduction of IIa with zinc afforded XII in almost quantitative yield. The electronic spectrum of XII, 271, 330 and 423 nm, is similar to those of IIa and X. The IR spectrum, 1765 and 1540 cm^{-1}, show the presence of a 4-membered ketone and *exo*-double bond. The NMR spectrum shows a singlet signal at 6·36 τ attributed to the two methylene protons. The correctness of the assignment was confirmed with using the deuterated compound XII-d_2, prepared by the reduction of IIa in methanol-d_1, which shows no signal at 6·36 τ. The reduction of IIa with sodium borohydride gave 2,3-bis(diphenylmethylene)cyclobutanol (XIII). The electronic spectrum of XIII, 259 and 359 nm, is similar to the previously reported data[1] of 1,2-bis(diphenylmethylene)cyclobutane, 260 and 357 nm and to that of IX, 262 and 369 nm. The NMR spectrum, 4·80 (m, CH, 1H), 6·96 (m, CH_2, 2H) and 8·15 τ (broad s, OH, 1H), is consistent with the structure XIII. All the spectral data are identical with those of the compound obtained by the sodium borohydride reduction of XII. Furthermore, XIII-d_2 prepared from XII-d_2 shows two doublets at 4·80 (CH) and 8·20 τ (OH) in a 1:1 integral ratio. Study on the reaction mechanism of the sodium borohydride reduction of IIa into XIII is in progress.

The monohalo derivative of II (XVII) was prepared by acid hydrolysis of 1-isopropoxy-2-halo-3,4-bis(diphenylmethylene)cyclobutene (XV) obtained by the reaction of I with isopropanolic potassium hydroxide. The heating of a mixture of Ia, potassium hydroxide, isopropanol and THF as described in the Experimental afforded XVa in practically quantitative yield. The structure of XVa was identified by the spectral data. The IR spectrum shows the following bands, 1675 (m), 1580 and 1570 (vs, unsplit doublet), 1260 (m), 1105 (m), 920 (m), 910 (m) and 840 cm^{-1} (m). The very strong band at 1580 and 1570 cm^{-1} can be assigned to the stretching of the isopropoxysubstituted *endo*-double bond of XV, since it has been known[4] that a double bond substituted with electron donating element such as O or N shows a strong doublet at relatively lower wavenumber region. Therefore, the medium band at 1675 cm^{-1} is assigned to the *exo*-double bond. Although the two medium bands at 1260 and 1105 cm^{-1} are assignable to vinyl ether and alkyl ether respectively, other ones are not clear. Of the two electronic absorption bands in chloroform, 281 and 315 nm, the former is comparable to those of various 1,2-dihalo-3,4-bis-(diphenylmethylene)cyclobutenes, 285–290 nm.[1] However, the latter is representative of XV and probably due to the conjugation of the isopropoxy. The NMR spectrum shows the presence of four phenyls and one isopropoxy.

Similar to the reaction of Ia, Ib was converted to XVb. The spectral data of XVb are shown in the Experimental. The transformation of I to XV may proceed by an addition-elimination process *via* XIV, as shown in Scheme 3.

Since both the XVa and XVb are sensitive to daylight even in the solid state, recrystallization was difficult. During the course of recrystallization from usual organic solvents, XV gradually turned into XVII. The effective preparative method of XVII was acid-catalyzed hydrolysis of XV. For example, the heating of a mixture of XVa, methanol and a small amount of conc hydrochloric acid, afforded XVIIa quantitatively. All the spectral data recorded for XVIIa are very similar to those of IIa. The IR spectrum in Nujol, 1765 (CO) and 1530 cm^{-1} (C═C), and the electronic spectrum in chloroform, 274, 342 and 453 nm are almost the same as those of IIa. The NMR spectrum of XVIIa is also comparable to those of IIa except the singlet signal of the methyne proton of XVIIa at 4·35 τ. The methyne proton signal was not observed for XVIIa–d obtained on treatment of XVa with DCl in D_2O–CH_3OD.

The bromine of XVIIa was replaced with the chlorine of sodium chloride by the procedure employed for IIa, and afforded XVIIb. The spectral data of the XVIIb produced are identical with those of the compound obtained by the acid-catalyzed hydrolysis of XVb. In acidic media, however, the halogen of XVII was not exchanged. For example, the hydrolysis of XVa with hydrochloric acid afforded XVIIa but not XVIIb. In a preliminary communication,[10] we assigned a cyclobutadiene epoxide structure and 3-diphenylmethyl-4-diphenylhalomethylcyclobutenedione structure to XV and XVII respectively. However, on the basis of the above data, it is clear that our original assignments were wrong.



Scheme 3

For XVII, some reactions similar to those of II were observed. The reduction of XVII with zinc afforded XII. The treatment of XVII with an equimolar amount of silver perchlorate afforded 4-diphenylmethylene-3-diphenylhydroxymethylcyclobut-2-enone (XVIII) in 52% yield. The spectral data of XVIII are similar to those of its bromo derivative (IVa). Especially, the electronic absorption band of XVIII, 280 nm is very similar to that of IVa, 277 nm. The IR spectrum, 3470 (OH), 1765 (CO), 1530 (C=C) and 835 cm^{-1} (=CH—), is consistent with the structure of XVIII. The olefinic hydrogen was identified by a singlet signal at 3·63 τ in the NMR spectrum. Further structural evidence for XVIII was obtained by the reactions with bromine and with methanol-sulfuric acid to afford SN2′ type reaction products XVIIa and 2-methoxy-3,4-bis(diphenylmethylene)cyclobutanone (XIX) respectively. The electronic spectrum of XIX, 272, 330 and 429 nm, is similar to that of II, X, XII or XVII. The IR spectrum, 1755 (CO), 1545 (C=C) and 1070 cm^{-1} (C—O—C) is also consistent with the structure XIX. The NMR spectrum shows two singlet signals at 4·74 and 6·25 τ attributed to methyne and methoxy protons respectively. The methoxyketone XIX was also obtained by the reaction of XVII with silver perchlorate in 80% yield. The difference of the reaction mode between the OH which attacks benzyl carbon and OMe which attacks ring carbon may be due to a steric factor. The reduction of XVIIa with sodium borohydride afforded XIII in almost a quantitative yield. Study of the reaction mechanism which is probably similar to that of the reduction of IIa to XIII, is also in progress. The electronic absorption spectra of the two methylenecyclobutenone derivatives IVa and XVIII have been discussed in a preliminary communication.[6]

EXPERIMENTAL

All m.ps were uncorrected. The IR spectra were recorded on a spectrophotometer IR-E of the Japan Spectroscopic Co. The Electronic spectra were recorded on a Hitachi spectrophotometer, model 124. The NMR spectra were recorded on a Japan Electron Optics Laboratory H-100 Spectrometer, in $CDCl_3$, using TMS as an internal standard. Mol wts were determined in benzene by a Hitachi Perkin–Elmer apparatus model 115.

Photooxidation of Ia. Under O_2, a stirred soln of Ia (5·4 g, 10 mmoles) in benzene (50 ml) was irradiated using a Toshiba Hg-lamp 100 UV-2 at room temp for 5 hr. A crystalline solid was collected by filtration and recrystallized from AcOEt to afford IIa as crimson prisms (2·8 g, 50%), m.p. 182 ~ 182·5°; λ_{max} (CH_3CN) nm (ε), 260 (20,800), 270 (20,800), 346 (9100) and 460 (13,900); ν_{max} (Nujol) cm^{-1}, 1770 (CO) and 1540 (C=C) and 825 (Found: C, 64·56; H, 3·47; mol wt, 568. Calcd for $C_{30}H_{20}OBr_2$: C, 64·74; H, 3·60%; mol wt, 556).

Heating of a mixture of IIa, acetonitrile and NaCl aq under reflux for 30 min afforded IIb, quantitatively. An analytical sample was obtained by the recrystallization from AcOEt, crimson prisms, m.p. 169 ~ 170°; ν_{max} (Nujol) cm^{-1}, 1775 (CO), 1540 (C=C) and 850 (Found: C, 76·71; H, 4·15. Calcd for $C_{30}H_{20}OCl_2$: C, 77·09; H, 4·28%).

Reaction of IIa *and silver fluoroborate in wet* CH_3CN. A soln of IIa (5·56 g, 10 mmoles), silver fluoroborate (1·95 g, 10 mmoles) and commercial CH_3CN (50 ml) was stirred at room temp for 10 min. After removal of AgBr, the organic layer was concentrated by the evaporation to *ca* 10 ml. A crystalline solid was collected and recrystallized from CH_3CN to yield III as green needles or prisms (3·71 g, 90%), m.p. 206 ~ 207°; λ_{max} (CH_3CN) nm (ε), 252 (11,200), 274 (12,900), 315 (sh) (6300), 465 (sh) (6200), 499 (12,000) and 620 (3100); ν_{max} ($CHCl_3$) cm^{-1}, 1750 with shoulders at 1770 and 1720 (CO) and 1550, 1520 (C=C). (Found: C, 87·15; H, 4·63; mol wt, 410. Calcd for $C_{30}H_{20}O_2$: C, 87·35; H, 4·89%; mol wt, 412).

Reaction of IIa *and silver fluoroborate in* 10% H_2O-CH_3CN *or* 10% H_2O-THF. A soln of IIa (5·56 g, 10 mmoles) and $AgBF_4$ (1·95 g, 10 mmoles) in 10% H_2O-CH_3CN (130 ml) was stirred at room temp for 1 hr. The AgBr formed was removed by filtration and the filtrate was concentrated to dryness. Recrystallization of the residue gave a mixture of the two crystalline forms, green needles and colorless prisms, which were separated mechanically. The green needles and colorless prisms were identified as III (1·01 g, 27%) and IVa (2·10 g, 44%) respectively by the comparison their spectral data with those of corresponding authentic samples, III prepared in the above experiment and IVa prepared according to the previously reported method.[6]

When the reaction was carried out in 10% H_2O-THF, III and IVa were obtained in 29 and 27% yields respectively.

Reaction of IIa *and silver perchlorate in wet* CH_3CN. A soln of IIa (5·56 g, 10 mmoles), silver perchlorate (2·07 g, 10 mmoles) and commercial CH_3CN (50 ml) was stirred for 10 min at room temp. The filtrate after removal of AgBr was concentrated to *ca* 10 ml. The crystals were filtered off and recrystallized from CH_3CN to afford red rhombs contaminated with a small amount of colorless needles. The two crystalline forms were separated mechanically. Each mass was purified by the recrystallization from CH_3CN. Of the two, red rhombs (3·64 g, 85%), m.p. 230° were identified as V; λ_{max} ($CHCl_3$) nm (ε), 249 (16,700), 315 (15,100) and 424 (9800); λ_{max} (Nujol) cm^{-1}, 1795 and 1755 (CO) and 1545 (C═C). (Found: C, 83·74; H, 4·77; Calcd for $C_{30}H_{20}O_3$: C, 84·09; H, 4·71%).

The IR spectral data (Nujol) of the colorless needles (*ca* 0·1 g) obtained by mechanical separation were: 1850 and 1840 (unsplit doublet, CO), 1780 (CO), 950, 920 and 900 cm^{-1}.

Oxidation of III *with* H_2O_2, $HClO_4$ *or* HNO_3. A soln of III (0·10 g) and 30% H_2O_2 (1 ml) in 1:1 AcOH–$CHCl_3$ (10 ml) was allowed to stand at room temp for 15 hr. The red rhombs which crystallized out were recrystallized from AcOEt to afford V (0·08 g, 77%). The IR and electronic spectral data of V were identical with those of an authentic sample prepared above.

By the heating under reflux of a mixture of III (0·15 g), CH_3CN (10 ml) and conc $HClO_4$ (1 ml) for 30 min, V (0·06 g, 39%) was obtained. When a mixture of III (0·15 g), CH_3CN (10 ml) and conc HNO_3 (1 ml) was heated under reflux for 10 min, V (0·04 g, 27%) was isolated.

Hydrolysis of V. A mixture of V (0·25 g), NaOH (0·05 g) and 20% aqueous acetone (30 ml) was heated under reflux for 2 hr. The crude crystals formed by addition of conc HCl (5 ml) to the mixture were washed with water, dried and recrystallized from EtOH to afford VI as pale yellow needles (0·16 g, 63%), m.p. 233 ~ 234°; λ_{max} (EtOH) nm (ε), 228 (20,300), 266 (11,700) and 320 (sh) (6800); ν_{max} (Nujol) cm^{-1}, 1695 and 1670 (unsplit doublet, CO). (Found: C, 80·40; H, 4·76; Calcd for $C_{30}H_{22}O_4$: C, 80·70; H, 4·97%).

Quinoxaline derivative of III (VIII). A soln of III (0·50 g) and *o*-phenylenediamine (0·15 g) in CCl_4 (50 ml) was stirred at room temp for 1 hr. The solid remaining after evaporation of the solvent was recrystallized from acetone to yield VIII as yellow needles (0·26 g, 73%), m.p. 240 ~ 241°; λ_{max} ($CHCl_3$) nm (ε), 276 (15,000) and 434 (13,000); ν_{max} (Nujol) cm^{-1}, 1628 (C═N). (Found: C, 89·66; H, 4·89. Calcd for $C_{36}H_{24}N_2$: C, 89·24; H, 4·96%).

Reduction of III by $NaBH_4$. To a soln of III (0·50 g) in EtOH (50 ml), large excess $NaBH_4$ (0·3 g) was added at room temp. After the exothermic reaction ceased, the crystalline mass was washed with water and then with EtOH. The dried crude product was recrystallized from iso-PrOH to yield IX as yellow needles (0·40 g, 80%), m.p. 224 ~ 225°; λ_{max} (EtOH) nm (ε), 262 (21,400) and 369 (17,500); ν_{max} (0·01 mole/l $CHCl_3$) cm^{-1}, 3630 (OH). (Found: C, 86·45; H, 5·70. Calcd for $C_{30}H_{24}O_2$: C, 86·51; H, 5·81%).

The diacetate of IX was prepared by heating a mixture of IX, Ac_2O, pyridine and acetone for 30 min, pale yellow needles, m.p. 197 ~ 198°; ν_{max} (Nujol) cm^{-1}, 1745 (CO), 1235 (ester); NMR τ, 2·75 (s, Ph, 10H), 3·20 (s, Ph, 10H), 3·76 (s, CH, 2H) and 8·53 (s, $COCH_3$, 6H). (Found: C, 81·36; H, 5·65. Calcd for $C_{34}H_{28}O_4$: C, 81·58; H, 5·64%).

Reaction of IIa *and* MeOH. A soln of IIa (0·5 g) in MeOH (30 ml) was heated under reflux for 1 hr. The crystalline solid remaining after evaporation of MeOH was recrystallized from acetone to afford X as orange red needles (0·3 g, 73%), m.p. 191 ~ 192°; λ_{max} ($CHCl_3$) nm (ε), 275 (11,500), 336 (3900) and 425 (7200); ν_{max} (Nujol) cm^{-1}, 1755 (CO), 1555 (C═C) and 1100 (C–O); NMR τ, 2·65 (m, Ph, 10H), 3·10 (m, Ph, 10H) and 6·55 (s, OCH_3, 6H). (Found: C, 83·52; H, 5·46. Calcd for $C_{32}H_{26}O_3$: C, 83·82; H, 5·57%).

When a soln of X in aqueous MeOH containing a catalytic amount of HCl was heated for 5 min, III was obtained in quantitative yield.

Reaction of III *and* MeOH. When a soln of III (0·5 g) in MeOH (100 ml) was allowed to stand at room temp for 15 days, X (0·18 g, 33%) crystallized as orange red needles, m.p. 191 ~ 192°. The diketone III reacted with MeOH in the presence of HCl. HCl was passed through a suspension of III (0·20 g) in MeOH (20 ml) for 5 min. This soln was then heated under reflux for 30 min. After cooling, X (0·19 g, 86%) crystallized out, m.p. 191 ~ 192°. Both products were identical with an authentic sample of X prepared from IIa (undepressed mixture m.p. and superimposable IR spectra).

Reaction of IVa *and* MeOH–H_2SO_4. A mixture of IVa (0·50 g), MeOH (20 ml) and five drops of conc H_2SO_4 was heated under reflux for 1 hr. After cooling, X (0·38 g, 83%) was collected by filtration, m.p. 191 ~ 192°. The structure of X was identified by mixed m.p. and the comparison of its IR spectrum with that of an authentic sample.

Reduction of IIa *by* Zn. A mixture of IIa (0·50 g), MeOH (60 ml) and Zn (2 g) was heated under reflux for 2 hr. After filtration, the MeOH soln was evaporated to dryness. The crude product was recrystallized from AcOEt to afford XII (0·31 g, 89%) as orange yellow needles, m.p. 183 ~ 184°; λ_{max} ($CHCl_3$) nm (ε), 271

(11.300). 330 (3600) and 423 (5900); ν_{max}(Nujol cm^{-1}. 1765 (CO). 1550 (C=C); NMR τ. 2·70 (m. Ph 10H). 3·18 (m. Ph. 10H) and 6·36 (s. CH_2 2H). (Found: C. 90·33; 5·35. Calcd for $C_{30}H_{22}O$: C. 90·44; H. 5·57%).

The NMR spectrum of XII-d_2. prepared by the reaction of IIa with Zn in MeOD. shows the signals. 2·71 (m. Ph. 10H) and 3·20 τ (m. Ph. 10H) but no signal of methylene proton at 6·36 τ.

Reduction of XII *and* XII-d_2 *by* $NaBH_4$. A soln of XII (0·50 g) and a large excess $NaBH_4$ (0·2 g) in 1:1 MeOH- THF (50 ml) was allowed to stand at room temp for 1 hr. The residue remaining after evaporation of solvent was decomposed with water. filtered. washed with water and dried. Recrystallization of the crude product from cyclohexane afforded XIII (0·45 g. 90%) as yellow needles. m.p. 187 ~ 188°; λ_{max} (EtOH) nm (ε). 259 (25.100) and 359 (20.700); ν_{max} (0·01 mole/l $CHCl_3$) cm^{-1}. 3580 (OH); NMR τ. 2·75 (m. Ph. 10H). 3·19 (s. Ph. 10H). 4·80 (broad t. CH. 1H). 6·96 (m. CH_2. 2H) and 8·15 (broad s. OH. 1H). (Found: C. 89·95; H. 5·88. Calcd for $C_{30}H_{24}O$: C. 89·96; H. 6·04%).

The NMR spectrum of XIII-d_2. prepared by $NaBH_4$ reduction of XII-d_2. was 2·78 (m. Ph. 10H). 3·20 (s. Ph. 10H). 4·80 (d. $J = 4$ Hz. CH. 1H) and 8·20 τ (d. $J = 4$ Hz. OH. 1H).

Reduction of IIa *by* $NaBH_4$. A mixture of finely powdered IIa (0·50 g). $NaBH_4$ (0·3 g) and MeOH (50 ml) was allowed to stand at room temp for 1 hr. The crude product formed by the addition of water was filtered off. washed with water and dried. Recrystallization from cyclohexane afforded XIII (0·33 g. 91%) as yellow needles. m.p. 185 ~ 186·5°. The IR spectrum of XIII was identified with that of an authentic sample.

Preparation of XV. A mixture of Ia (0·50 g). KOH (1·5 g) and iso-PrOH (20 ml) was heated under reflux for 2 hr. After the mixture was decomposed with water. the crystals were washed with water and then MeOH. and dried to afford XVa (0·45 g. 96%) as colorless fine needles. m.p. 186 ~ 188° (dec); λ_{max} ($CHCl_3$) nm (ε). 281 (32.300) and 315 (sh) (24.300); ν_{max} ($CHCl_3$) cm^{-1}. 1675 (C=C). 1580 and 1570 (unsplit doublet. C=C). 1260 (=C—O—). 1105 (C—O—C). 1040. 920. 910 and 840 (can not be assigned); NMR τ. 2·66 (d. Ph. 10H). 3·18 (m. Ph. 10H). 4·98 (q. $J = 6$ Hz. CH. 1H) and 8·99 (d. $J = 6$ Hz. CH_3. 6H). (Found: C. 75·15; H. 5·19; mol wt. 514. Calcd for $C_{33}H_{27}OBr$: C. 76·32; H. 5·20%; mol wt. 519).

When the same reaction was employed for Ib. XVb (97%) was obtained as colorless needles. m.p. 190°. ν_{max} (Nujol) cm^{-1}. 1670 (*exo*-C=C). 1580 and 1565 (unsplit doublet. *endo*-C=C). 1270 (=C—O—). 1110 (C—O—C). 1040. 920. 910 and 845 (can not be assigned). (Found: C. 81·15; H. 5·55. Calcd for $C_{33}H_{27}OCl$: C. 82·19; H. 5·69%).

In the case of large scale preparation of XV. it was convenient to add THF to the reaction. Since both the XVa and XVb were too unstable to purify by recrystallization. the analytical data was not satisfactory.

Acid-catalyzed hydrolysis of XVa *and* XVb. A mixture of XVa (3·0 g). 10% aqueous EtOH (20 ml) and conc HCl (3 ml) was heated under reflux for 30 min. After cooling. the crystalline solid formed was washed successively with water and EtOH and dried. Recrystallization from AcOEt afforded XVIIa (2·6 g. 94%) as orange red hexagonals m.p. 202 ~ 203°; λ_{max} ($CHCl_3$) nm (ε). 274 (30.300). 342 (9500) and 453 (13.300); ν_{max} (Nujol) cm^{-1}. 1765 (CO) and 1530 (C=C); NMR τ. 2·60 (d. Ph. 10H). 3·13 (d. Ph. 10H) and 4·35 (s. CH. 1H). The NMR spectrum of XVIIa-d. prepared by the hydrolysis of XVa with DCl in D_2O—MeOD. shows only aromatic protons but not a methyne proton at 4·35 τ. (Found: C. 75·42; 4·22; mol wt. 483. Calcd for $C_{30}H_{21}OBr$: C. 75·47; H. 4·40%; mol wt. 477).

The hydrolysis of XVb by the same procedure employed for XVa. afforded XVIIb (95%) as orange red hexagonals. m.p. 201 ~ 202°; ν_{max} (Nujol) cm^{-1}. 1770 (CO) and 1530 (C=C). (Found: C. 82·99; H. 4·66. Calcd for $C_{30}H_{21}OCl$: C. 83·24; H. 4·85%).

The spectral data of the compound obtained by the reaction of XVIIa and NaCl aq under the conditions used for IIa. are identical with those of the XVIIb produced.

Reduction of XVIIa *by* Zn. By the procedure employed for the reduction of IIa with Zn. XVIIa was reduced to XII (90%). The structure of XII was identified by the comparison of its IR spectrum with an authentic sample derived from IIa.

Reduction of XVIIa *with* $NaBH_4$. The treatment of XVIIa with $NaBH_4$ in MeOH under the conditions employed for IIa. afforded XIII (85%). The structure of XIII was identified by comparison of its IR spectrum with an authentic sample derived from IIa or XII.

Reaction of XVII *with silver perchlorate in* 10% H_2O—THF. A soln of XVIIa (0·24 g. 0·5 mmole). silver perchlorate (0·11 g. 0·5 mmoles) in 10% aqueous THF (20 ml) was stirred at room temp for 30 min. The mixture was diluted with ether (150 ml). The ether soln was washed successively with NaCl aq. water and dried over Na_2SO_4. The oily residue after evaporation of the solvent was crystallized by the addition of EtOH (2 ml). Recrystallized from AcOEt yielded XVIII (0·11 g. 52%) as colorless prisms or needles. m.p. 163 ~ 164°; λ_{max} (EtOH) nm (ε). 280 (21.400); ν_{max} ($CHCl_3$) cm^{-1}. 3520 (OH). 1767 (CO). 1530 (C=C). 1040. 1025 (OH). 970 and 835 (=CH—); NMR τ. 2·6 ~ 3·3 (m. Ph. 20H). 3·63 (s. =CH. 1H) and 8·11

(s. OH. 1H). (Found: C. 86·79; H. 5·17; mol wt. 425. Calcd for $C_{30}H_{22}O_2$: C. 86·93; H. 5·35%; mol wt. 414·5).

Similar to the reaction of XVIIa, XVIIb reacted with silver perchlorate and afforded XVIII (50%).

Reaction of XVIII *with* Br_2 *and with* MeOH- H_2SO_4. To a soln of XVIII (0·21 g, 0·5 mmole) in $CHCl_3$ (5 ml), two drops of Br_2 was added. The crude product on evaporation of the solvent was recrystallized from AcOEt to afford XVIIa (0·18 g, 80%), its IR spectrum was identical with that of an authentic specimen.

A soln of XVIII (0·21 g, 0·5 mmole) in MeOH (5 ml) containing one drop of conc H_2SO_4 was heated under reflux for 30 min. The crystals formed by cooling the mixture were recrystallized from EtOH--AcOEt to yield XIX (0·15 g, 70%) as orange needles, m.p. 178 ~ 180°; λ_{max} (EtOH) nm (ε). 272 (23.200), 330 (7800) and 429 (13.900); ν_{max} (Nujol) cm^{-1}. 1755 (CO), 1545 (C=C) and 1070 (C--O--C); NMR τ. 2·70 (d. Ph. 10H), 3·16 (d, Ph. 10H), 4·74 (s. CH. 1H) and 6·75 (s. OCH_3. 3H). (Found: C. 86·31; H. 5·72. Calcd for $C_{31}H_{24}O_2$: C. 86·89; H. 5·65%).

Reaction of XVIIa *with silver perchlorate in* 10% MeOH- THF. A mixture of XVIIa (0·48 g, 1 mmole), silver perchlorate (0·21 g, 1 mmole) and 10% MeOH - THF (15 ml) was stirred at room temp for 30 min. The mixture was diluted with ether (200 ml). The ether soln was washed successively with NaCl aq and water and dried over Na_2SO_4. The oily mass after evaporation of the solvent was crystallized by the addition of EtOH (2 ml). The crystals were recrystallized from EtOH- AcOEt to afford XIX (0·34 g, 80%), m.p. 178 ~ 180°. This compound was identical with an authentic sample of XIX derived from XVIII by superimposable IR spectra.

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