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The Formation of Substituted Quinazolines from Substituted Indoles by the Sensitized Photo-oxygenation in the Presence of Ammonium Acetate[1]

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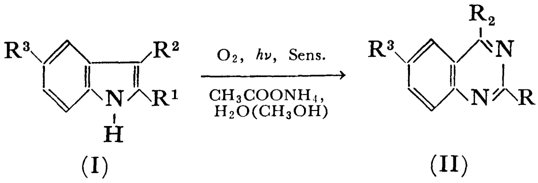
2,4-Di- and 2,4,6-trisubstituted quinazolines (II) were prepared from 2,3-di- and 2,3,5-trisubstituted indoles (I) respectively by the sensitized photo-oxygenation in aqueous methanol in the presence of ammonium acetate or by fusion with ammonium acetate after the photo-oxygenation. Chemical evidences that II was produced *via* the hydroperoxide (III) of the indole and then the dicarbonyl compound (IV) were provided.

In our previous paper[2] we reported that 2,4,6-triaryl-*s*-triazines were produced from 2,4,5-triarylimidazoles by the sensitized photo-oxygenation in methanol in the presence of ammonium acetate and the reaction proceeded *via* the hydroperoxides which afforded the triazines by the reaction with ammonium acetate. Although the formation of 2,4-dioxo-1,2,3,4-tetrahydroquinazoline from indole and that of 2-phenyl-4-oxo-3,4-dihydroquinazoline from 2-phenylindole, similar to that of triaryl-*s*-triazine from triarylimidazole, on irradiation with sunlight in ethanol in the presence of oxygen and ammonia have been reported,[3] no investigations have been carried out similar reactions for 2,3-di- and 2,3,5-trisubstituted indoles. The present paper deals with the formation of 2,4-di- and 2,4,6-trisubstituted quinazolines from the corresponding 2,3-di- and 2,3,5-trisubstituted indoles by sensitized photo-oxygenation in the presence of ammonium acetate and the reaction mechanism of the ring enlargement.

Results and Discussion

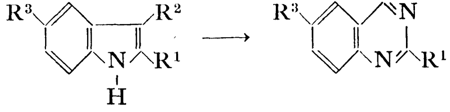
Indoles (Ia, Ib, Ic, Id listed in Table 1) were transformed to quinazolines (IIa, IIb, IIc, IId) respectively by sensitized photo-oxygenation in aqueous methanol in the presence of ammonium acetate. The reaction was carried out at room temperature and completed by boiling the methanolic solution. The procedure was similar to that for the formation of trisubstituted triazines from trisubstituted imidazoles.[2] The time-course of the ring enlargement was followed by UV spectrum and thin layer chromatography. The spectrum and chromatogram changed with the formation of the quinazoline (II) *via* the hydroperoxide (III) and the dicarbonyl compound (IV). Indoles (Ie and If) which have phenyl groups at the 2- and 3-positions did not give quinazolines by the same procedure as that for Ia—Id. These quinazolines (IIe and IIf), however, were obtained by fusion of the solid residue after removal of the solvent from the reaction mixture of the sensitized photo-oxygenation of Ie and If, with ammonium acetate at about 180 °C, respectively.



(I) (II)

When about 20 vol% of water was added into methanol, the reaction rate from I to II was increased because of the acceleration of the formation of IV from III. The short reaction time was convenient to avoid a formation of fair amounts of brown oily products by prolonged heating of the reaction mixture in a methanolic solution containing trace amounts of water after the formation of III from I. The yields and melting points of II are shown in Table 1. Ethanol, *n*-propyl alcohol and acetone which contained water were also usable as the solvent.

Table 1. 2,4-Di- and 2,4,6-trisubstituted quinazolines (II) from 2,3-di- and 2,3,5-trisubstituted indoles (I)



(I) (II)

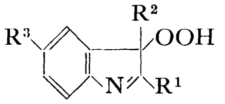
R^1	R^2	R^3			II	
					Mp °C	Yield %[a]
CH_3	CH_3	CH_3	Ia →	IIa	54— 55	67
CH_3	CH_3	Cl	Ib	IIb	108—109.5	72
CH_3	CH_3	OCH_3	Ic	IIc	109—110	44
C_6H_5	CH_3	H	Id	IId	85— 87 (90)[4,5]	65
C_6H_5	C_6H_5	H	Ie	IIe	118—119 (119—120)[6,7]	70
C_6H_5	C_6H_5	CH_3	If	IIf	177—179 (177)[7]	53

a) In methanol containing 20 vol% of water. Reaction conditions are shown in the experimental part.

It was reported[8,9] that several substituted indoles including Ia, Ib and Ic exhibited chemiluminescence on oxidation in basic solutions and the mechanism of the chemiluminescence reaction involved the primary formation of radicals of the indoles and then oxygenation of the radicals to hydroperoxides by molecular oxygen. The mechanism of the chemiluminescence is similar to that of imidazole derivatives.[10] Similarities between indoles and imidazoles in both ring enlargement reaction and mechanism of chemiluminescence reaction suggested that in the ring enlargement reaction of the indole (I) hydroperoxides are also intermediates. Hydroperoxides (IIIa—IIIf in Table 2) (2,3-di- and 2,3,5-trisubstituted-3-hydroperoxyindolenins) were prepared to examine the reaction with ammonium acetate in aqueous methanol. Hydroperoxides (IIIa—IIId) were prepared by autoxidation or by sensitized photo-oxygenation of indoles (Ia—Id) whereas IIIe and IIIf were obtained only by sensitized photo-oxygenation of Ie and If. Hydroperoxide (IIIf) was also obtained by reaction of If and singlet oxygen prepared from hydrogen peroxide and sodium hypochlorite.[11)] These facts suggested that singlet oxygen was probably involved in oxygenation of Ie and If.

N-Methyl-2,3-diphenylindole which did not transform to a quinazoline derivative by the same procedure as that for Ie and If did not give a hydroperoxide by the sensitized photo-oxygenation. This result shows that hydrogen on nitrogen of the indole (I) is necessary for the oxygenation and also for the ring enlargement.

TABLE 2. HYDROPEROXIDES OF 2,3-DI- AND 2,3,5-TRI-SUBSTITUTED INDOLES (III)


(III)

	R¹	R²	R³	Mp (°C)	Yield (%) A	Yield (%) B
IIIa	CH_3	CH_3	CH_3	111.5—112.5 (111.5)[12)]	76	88
IIIb	CH_3	CH_3	Cl	112—113	60	89
IIIc	CH_3	CH_3	OCH_3	108—109 (109)[13)]	59	
IIId	C_6H_5	CH_3	H	146—148 (148—152)[14)]	82	
IIIe	C_6H_5	C_6H_5	H	157—158		85
IIIf	C_6H_5	C_6H_5	CH_3	175—176		70

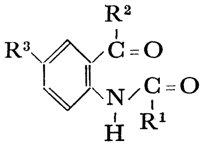
A: Autoxidation, B: Sensitized photo-oxygenation

By treatment of IIIa, IIIb and IIId with ammonium acetate in aqueous methanol at room temperature or under reflux IIa, IIb and IId were produced respectively (Table 3). Hydroperoxides IIIe and IIIf did not give the corresponding quinazolines by the same procedure, but produced dicarbonyl compounds, 2-benzamidobenzophenone (IVe) and 2-benzamido-5-methylbenzophenone (IVf) as shown in Table 4, respectively, which were transformed to IIe and IIf by fusion with ammonium acetate at about 180 °C. The method of preparation of quinazoline derivatives from dicarbonyl compounds (VI, R¹, R², R³: H, alkyl, aryl) by heating with ammonia in ethanol under pressure or fusion with ammonium acetate is known as Bischler's method.[6,15)] When the sensitized photo-oxygenation of Ia and Id in aqueous methanol containing ammonium acetate was stopped before the reaction was completed, dicarbonyl compounds IVa and IVd (Table 4) were isolated with a small amount of IIa and IId, respectively. These facts suggested that dicarbonyl compound (IV) was probably formed from the hydroperoxide (III) and then transformed to the quinazoline (II) by ring closure with ammonia. In order to confirm this reaction process, IIIa, IIIb, IIId, IIIe and IIIf were heated in aqueous methanol and IVa, IVb, IVd, IVe and IVf (Table 4) were obtained. Water was necessary for the transformation of the hydroperoxides to the dicarbonyl compounds. The reaction rate was accelerated with increasing amounts of water in methanol and was very fast on boiling in water. The need of water in methanol for the ring enlargement of the indole (I) to the quinazoline (II) is considered to be associated with the formation of the dicarbonyl compound (IV) by hydrolytic reaction of hydroperoxide (III).

TABLE 3. YIELDS OF QUINAZOLINES (II) FROM HYDROPEROXIDES (III)

III		II	Yield (%)
IIIa	→	IIa	60
IIIb		IIb	62
IIId		IId	86
IIIe		IIe	60
IIIf		IIf	55

TABLE 4. DICARBONYL COMPOUNDS (IV) FROM HYDROPEROXIDES (III)


(IV)

	R¹	R²	R³	Mp °C	Yield (%)
IVa	CH_3	CH_3	CH_3	123—124 (123—124)[16)]	84
IVb	CH_3	CH_3	Cl	133—134 (134—134.5)[12)]	70
IVd	C_6H_5	CH_3	H	93.5— 95 (98)[14)]	76
IVe	C_6H_5	C_6H_5	H	81— 82 (80.5)[13)]	64
IVf	C_6H_5	C_6H_5	CH_3	114—116 (114—117)[16)]	92

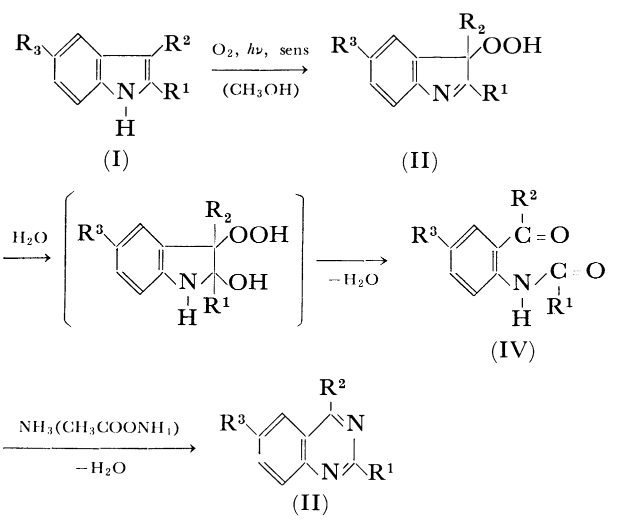
As shown in Table 5, IIa, IIb and IId were obtained by treating IVa, IVb and IVd, respectively, with ammonium acetate in methanol or aqueous methanol at room temperature or under boiling, whereas IIe and IIf which were not obtained by the same procedure were obtained by fusion of IVe and IVf with ammonium acetate at about 180 °C. Quinazolines (IIa, IIb and IId) were also obtained by fusion of IVa, IVb and IVd with ammonium acetate.

From these results the mechanism of the ring enlargement reaction of 2,3-di- and 2,3,5-trisubstituted in-

TABLE 5. YIELDS OF QUINAZOLINES (II) FROM DICARBONYL COMPOUNDS (IV)

IV		II	Yield (%)
IVa	→	IIa	86
IVb		IIb	88
IVd		IId	89
IVe		IIc	69
IVf		IIf	70

doles (I) to 2,4-di- and 2,4,6-trisubstituted quinazolines (II) by sensitized photo-oxygenation in the presence of ammonium acetate is concluded to be shown by the following scheme:



In the transformation of triphenylimidazole to triphenyl-*s*-triazine the carbonyl compound, *N*,*N*′-dibenzoylbenzamidine, did not give the triazine by the reaction with ammonium acetate in a methanolic solution and even by fusion with ammonium acetate at about 180 °C. These results seem to show that the process of the ring enlargement of substituted indoles differs in part from that of substituted imidazoles.

Experimental

All the melting points are uncorrected. The IR spectra were obtained in a JASCO IR-G spectrophotometer. The UV spectra were measured by a Hitachi 124 spectrophotometer.

Preparation of Substituted Indole (I). All the indoles examined were prepared by the method described in the literatures.[14,17,18,19]

2,3,5-Trimethylindole (Ia)[17]: Colorless plates (from ethanol-water), mp 118—119 °C. Found: C, 82.91; H, 8.23; N, 8.58%. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80%.

2,3-Dimethyl-5-chloroindole (Ib)[17]: Colorless plates with luster (from benzene), mp 142—144 °C. Found: C, 66.94; H, 5.56; N, 7.86; Cl, 19.64%. Calcd for $C_{10}H_{10}NCl$: C, 66.86; H, 5.61; N, 7.80; Cl, 19.73%.

2,3-Dimethyl-5-methoxyindole (Ic)[17]: Colorless needles (from ethanol and then from petroleum ether), mp 104—106 °C. Found: C, 75.76; H, 7.43; N, 8.05%. Calcd for $C_{11}H_{13}NO$: C, 75.48; H, 7.48; N, 7.99%.

2-Phenyl-3-methylindole (Id)[14]: Pale brown prisms (from benzene), mp 88—90 °C. Found: C, 87.28; H, 6.51; N, 6.71%. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76%.

2,3-Diphenylindole (Ie)[18]: Colorless prisms (from benzene ligroin), mp 123.5—124 °C. Found: C, 89.33; H, 5.64; N, 5.11%. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61; N, 5.20%.

2,3-Diphenyl-5-methylindole (If)[18]: Colorless needles (from acetone-ligroin), mp 158—159 °C. Found: C, 89.10; H, 6.06; N, 5.00%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%.

N-*Methyl-2,3-diphenylindole*: Colorless needles (from acetic acid), mp 135—136 °C (137 °C[19]). Found: C, 88.99; H, 6.06; N, 4.82%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%. This compound did not give a hydroperoxide and also a quinazoline derivative by the same procedure as those for the other indoles.

Formation of the Quinazoline (II) by Sensitized Photo-oxygenation of the Indole (I) in the Presence of Ammonium Acetate. General Procedure. An aqueous methanolic solution (containing 20 vol% of water) of indoles (Ia, Ib, Ic, Id) which contained ammonium acetate and methylene blue as a sensitizer was irradiated with two incandescent lamps (300 W) for 1—10 hr under bubbling oxygen at room temperature or was refluxed for 1 hr after the irradiation. The solvent was removed under reduced pressure and the residue was extracted with ether. The ether extracts were washed with aqueous sodium carbonate and with water for removing methylene blue and dried over sodium sulfate. Quinazolines IIe and IIf were formed by fusion of the products obtained by sensitized photo-oxygenation with ammonium acetate at about 180 °C.

2,4,6-Trimethylquinazoline (IIa): Ammonium acetate (5 g) was added to the aqueous methanolic solution (300 ml) of Ia (600 mg). The mixture was irradiated for 10 hr at room temperature or for about 1 hr and then refluxed for 1 hr. The brown residue after removal of ether from ether extract was chromatographed on an alumina column with benzene and *n*-hexane (1 : 1). The elute was evaporated and the remaining product was recrystallized from petroleum ether. Colorless prisms. Found: C, 76.72; H, 7.05; N, 16.30%. Calcd for $C_{11}H_{12}N_2$: C, 76.70; H, 7.02; N, 16.28%. λ_{max}^{EtOH} nm (ε): 227 (1.56×10^4), 259 (1.0×10^3), 315 (7.0×10^2). IR(KBr): 1625, 1570, 1560, 1510, 1498, 880, 827 cm^{-1}.

2,4-Dimethyl-6-chloroquinazoline (IIb): Ammonium acetate (5 g) was added to the aqueous methanolic solution (300 ml) of Ib (500 mg) and the resulting solution was irradiated for 7 hr. The product obtained by removal of the solvent from ether extract was recrystallized from ethanol. Colorless needles. Found: C, 62.38; H, 4.89; N, 14.51; Cl, 17.69%. Calcd for $C_{10}H_9N_2Cl$: C, 62.33; H, 4.71; N, 14.55; Cl, 18.41%. λ_{max}^{EtOH} nm (ε): 227 (9.1×10^3), 256 (2.2×10^3), 315 (1.4×10^3). IR(KBr): 1570, 1550, 1480, 865, 835, 805, 670 cm^{-1}.

2,4-Dimethyl-6-methoxyquinazoline (IIc): The aqueous methanol solution (300 ml) of Ic (600 mg) was treated by the same procedure as that in the case of formation of IIa. IIc was obtained as colorless needles by recrystallization from a mixture of ether and acetone. Found: C, 69.82; H, 6.42; N, 14.89%. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.89%. λ_{max}^{EtOH} nm (ε): 232 (2.1×10^4), 247 (2.6×10^3), 256 (2.3×10^3), 318 (1.9×10^3), 335 (1.9×10^3). IR(KBr): 1625, 1572, 1560, 1500, 845, 835 cm^{-1}.

2-Phenyl-4-methylquinazoline (IId): The aqueous methanol solution (200 ml) of Id (200 mg) was treated by the same procedure as that in the case of formation of IIa. IId was obtained as colorless plates by recrystallization from ethanol. Found: C, 81.58; H, 5.49; N, 12.33%. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72%. λ_{max}^{EtOH} nm (ε): 260 (2.9×10^4), 280 (1.0×10^4), 317 (3.4×10^3). IR(KBr): 1620, 1575, 1500, 1495, 780, 750, 704 cm^{-1}.

IId was also prepared by using acetone containing 20 vol % of water with 40% yield.

2,4-Diphenylquinazoline (IIe): Ammonium acetate (5 g) was added to the aqueous solution (300 ml) of Ie (500 mg) and the resulting solution was irradiated for 1 hr and then refluxed for 1 hr. The residue obtained by removal of the solvent was heated at 180 °C for 1.5 hr and then extracted with ether. The residue obtained by evaporation of the solvent was recrystallized from ethanol. Colorless prisms. Found: C, 85.00; H, 5.05; N, 9.81%. Calcd for $C_{20}H_{14}N_2$: C, 85.07; H, 5.00; N, 9.93%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 224 (1.36×10^4), 248 (1.27×10^4), 3.08 (9.6×10^3). IR(KBr): 1615, 1560, 1539, 1489, 770, 750, 695 cm^{-1}.

IIe was also obtained in *n*-propyl alcohol containing 20 vol% of water. The alcoholic solution of Ie (200 mg in 200 ml) was irradiated for 5 hr in the presence of methylene blue as a sensitizer under a stream of oxygen. After the solvent was removed from the solution, ammonium acetate (5 g) was added to the residue. The mixture was heated at 180 °C for 1.5 hr and IIe was obtained with 67% yield by the same procedure as that in the methanolic solution.

2,4-Diphenyl-6-methylquinazoline (IIf): The aqueous methanol solution (300 ml) of If (500 mg) was treated by the same procedure as that in the case of formation of IIe. IIf was obtained as colorless prisms by recrystallization from ethanol. Found: C, 85.02; H, 5.50; N, 9.41%. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 266 (1.37×10^4), 335 (1.3×10^3), 352 (1.3×10^3). IR(KBr): 1624, 1560, 1540, 1492, 840, 790, 770, 705 cm^{-1}.

IIf was also obtained with 55% yield in *n*-propyl alcohol containing 20 vol% of water.

Preparation of the Hydroperoxide (III). The hydroperoxide (III) was prepared by autoxidation (Method A)[12,13] or by sensitized photo-oxygenation (Method B). The yields and melting points of III are shown in Table 2.

Method A: A trace amount of benzoyl peroxide was added to a warm solution of indole (I) (200—300 mg in 60—80 ml of petroleum ether). Crystalline hydroperoxide began to deposit from the solution after about 1 hr. The solution was left to stand for 4 hr in a refrigerator, and the crystalline hydroperoxide was obtained. These hydroperoxides liberated iodine from potassium iodide and showed an IR absorption at near 2800 cm^{-1} due to a stretching vibration of -OOH.

Method B: A methanolic solution of the indole (I) was irradiated with two incandescent lamps (300 W) in the presence of methylene blue as a sensitizer under oxygen stream at 5—10 °C for 1 hr. The residue obtained by removing the solvent was extracted with ether. The ether solution was washed with water to remove methylene blue. The solution was dried over sodium sulfate. Crude hydroperoxide obtained by removing the solvent under reduced pressure. Although it was reported[13] that indole derivatives having phenyl group at the 3-position resist to the action of oxygen, IIIe and IIIf were obtained by sensitized photo-oxygenation.

IIIa, IIIe and IIIf were also obtained in ethanol.

2,3,5-Trimethyl-3-hydroperoxyindolenin (IIIa): Colorless prisms (from ethyl acetate-petroleum ether). Found: C, 69.07; H, 6.81; N, 7.32%. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 217 (2.57×10^4), 222 (2.68×10^4), 261 (6.0×10^3).

2,3-Dimethyl-5-Chloro-3-hydroperoxyindolenin (IIIb): Colorless needles (from ethyl acetate-petroleum ether). Found: C, 56.93; H, 4.79; N, 6.41; Cl, 17.44%. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62; Cl, 16.75%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 216(1.14×10^4), 219 (1.18×10^4), 261 (3.2×10^3).

2,3-Dimethyl-5-methoxy-3-hydroperoxyindolenin (IIIc): Pale gray prisms (from ethyl acetate-petroleum ether). Found: C, 63.92; H, 6.30; N, 6.81%. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 232 (1.13×10^4), 277 (4.4×10^3), 311 (2.4×10^3).

2-Phenyl-3-methyl-3-hydroperoxyindolenin (IIId): Colorless needles (from ethyl acetate-petroleum ether). Found: C, 74.93; H, 5.53; N, 5.77%. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 238 (1.3×10^4), 245 (1.2×10^4), 314 (1.0×10^4).

2,3-Diphenyl-3-hydroperoxindolenin (IIIe): Colorless prisms (from acetone-ligroin). Found: C, 79.72; H, 5.08; N, 4.53%. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 222 (9.0×10^3), 250 (8.7×10^3), 317 (6.13×10^3).

2,3-Diphenyl-5-methyl-3-hydroperoxyindolenin (IIIf): Colorless prisms (from acetone-ligroin). Found: C, 79.88; H, 5.50; N, 4.36%. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44%. $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 254 (5.6×10^3), 330 (4.0×10^3).

The hydroperoxide (IIIf) was also obtained by reaction of If with singlet oxygen which was produced by the method of Foote and Wexler.[11] To a methanolic solution (180 ml) of If (1.08 g) hydrogen peroxide (30%, 20 ml) was added. The solution was stirred in nitrogen atmosphere at about 10 °C, and 150 ml of 0.3 M sodium hypochlorite solution was added in 90 min. After the solution was left to stand for 1 hr at 0—5 °C, the solution was diluted with water and extracted with ether. The ether solution was dried over sodium sulfate. Yellowish oil remained by removing ether under reduced pressure was recrystallized from a mixture of ether and ethyl acetate.

Influence of an Amount of Water in Methanol for the Reaction Rate from IIIa to IVa. When a solution of IIIa (100 mg in 40 ml) in dehydrated methanol was allowed to stand for 20 hr and then refluxed for 5 hr, no change was observed by UV spectrum and thin layer chromatogram. In a methanolic solution containing about 1% of water, IIIa was changed to IVa in part by refluxing the solution for 8 hr. In an aqueous methanolic solution containing 20 vol% of water, IIIa was changed to IVa by refluxing for 0.5 hr. In boiling water, the change of IIIa to IVa came to an end in a few minutes.

Preparation of the Dicarbonyl Compound (IV). A methanolic solution (containing 20 vol% of water) (40 ml) of the hydroperoxide (III) (100 mg) was heated on a water bath for 0.5 hr. The solvent was removed under reduced pressure and the brown oily residue was recrystallized from *n*-hexane (in the case of IVa) or ethanol (in the cases of IVb, IVd, IVe, IVf). Their analytical values were satisfactory for the formulas corresponding to the dicarbonyl compounds. The yields and melting points are shown in Table 4.

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