This article was downloaded by: ["University at Buffalo Libraries"]
On: 07 October 2014, At: 11:37
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Oxidative Conversion of 3-Alkoxyfurans to 2-Hydroxy-3(2H)-furanones and 2-Hydroxy-2-butene-1,4-diones with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Phenyltrimethylammonium Tribromide (PTAB) in t-BuOH

Shinsei Sayama [a]
[a] Department of Chemistry, Fukushima Medical University, Hikariga-oka, Fukushima, Japan

Published online: 10 Sep 2007.

To cite this article: Shinsei Sayama (2007) Oxidative Conversion of 3-Alkoxyfurans to 2-Hydroxy-3(2H)-furanones and 2-Hydroxy-2-butene-1,4-diones with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Phenyltrimethylammonium Tribromide (PTAB) in t-BuOH, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:18, 3067-3075, DOI: 10.1080/00397910701543036

To link to this article: http://dx.doi.org/10.1080/00397910701543036

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthetic Communications®, 37: 3067–3075, 2007

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701543036

Oxidative Conversion of 3-Alkoxyfurans to 2-Hydroxy-3(2*H*)-furanones and 2-Hydroxy-2-butene-1,4-diones with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Phenyltrimethylammonium Tribromide (PTAB) in *t*-BuOH

Shinsei Sayama
Department of Chemistry, Fukushima Medical University, Hikariga-oka,
Fukushima, Japan

Abstract: 2-Alkoxy-1,3,4-triphenylfurans were oxidized to 3-alkoxy-2,4,5-triphenyl-2-butene-1,4-diones with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in *t*-BuOH. In contrast, various 3-alkoxy-2,4,5-triphenylfurans were directly converted to 2-hydroxy-3(2*H*)-furanone with phenyltrimethylammonium tribromide (PTAB) in *t*-BuOH. The oxidative ring opening of 3-alkoxy-2,5-diphenylfurans to *cis*-2-hydroxy-2-butene-1,4-dione was also accomplished with PTAB in *t*-BuOH under the same reaction conditions.

Keywords: 3-alkoxyfuran, DDQ, 2-hydroxy-2-butene-1,4-dione, 2-hydroxy-3(2*H*)-furanone, phenyltrimethylammonium tribromide, *t*-BuOH

Furans have been expected to be key intermediates for the synthesis of various natural products containing cyclopentenone, furanone, and enedione moieties, because of having latent functionalities of enedione and lactone.[1–5] Therefore, synthetic methods for the 3-furanone and 2-alkoxy-2-butene-1,

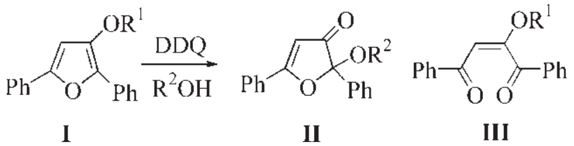
Received in Japan January 29, 2007

Address correspondence to Shinsei Sayama, Department of Chemistry, Fukushima Medical University, Hikariga-oka, Fukushima 960-1295, Japan. E-mail: ssayama@fmu.ac.jp

4-(L40), dione (L46) skeletones have been developed.[6–9] The conversion of furans to enediones was achieved by using oxidative reagents such as pyridinium chlorochromate (PCC), *m*-chloroperbenzoic acid (*m*CPBA), magnesium monoperoxyphtalate, dioxirane, methyltrioxorhenium/urea hydrogen peroxide, and $Mo(CO)_6$/cumyl hydroperoxide.[10–18] Commercially available phenyltrimethylammonium tribromide (PTAB) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are easy to handle and are useful for the oxidation of organic compounds to maintain the desired stoichiometry as well as other oxidizing reagents.[19,20] In a previous article, the conversion of 3-alkoxyfurans to 2-alkoxy-2-butene-1,4-diones was reported with PTAB in dimethyl sulfoxide (DMSO) or DDQ in CH_2Cl_2, respectively.[20] Because 3-alkoxyfurans were smoothly transformed to various 2-alkoxy-3(2*H*)-furanones with PTAB in alcohols, there has been much interest in the oxidation of 3-alkoxyfurans with DDQ in alcohols in comparison with that of PTAB. The oxidation of 3-alkoxyfurans with DDQ or PTAB in *t*-BuOH was subsequently found to afford 2-hydroxy-3(2*H*)-furanone and 2-hydroxyenediones. We report the results of our studies concerning the oxidation of 3-alkoxyfurans to hydroxyfuranone and hydroxyenedione with DDQ or PTAB in *t*-BuOH.

At first, the oxidation of 3-alkoxy-2,5-diphenylfurans (**1**, **4**) was carried out with DDQ in various alcohols at room temperature in comparison with that of PTAB. The results are summarized in Table 1. The oxidation of alkoxyfurans (**1**, **4**) with DDQ in ethyl alcohol or propyl alcohol afforded 2-ethoxy- or 2-propoxy-3(2*H*)-furanones (**2**, **3**) in good yields (runs 1–3).[20]

Table 1. Reaction of 3-alkoxyfurans with DDQ in alcohol[a]



Run	I	R^1	R^2OH/R^2	Time/(h)	II	(%)	III	(%)
					Products, yield			
1	**1**	C_2H_5	C_2H_5	39	**2**	86		
2	**1**	C_2H_5	C_3H_7	37	**3**	90		
3	**4**	C_3H_7	C_3H_7	24	**3**	88		
4	**1**	C_2H_5	*t*-C_4H_9	14			**5**	93
5	**6**	CH_3	*t*-C_4H_9	22			**7**	95
6	**4**	C_3H_7	*t*-C_4H_9	14			**8**	92
7	**9**	C_3H_7	*t*-C_4H_9	21			**10**	94
8	**11**	C_4H_9	*t*-C_4H_9	20			**12**	95
9	**13**	*i*-C_4H_9	*t*-C_4H_9	15			**14**	90

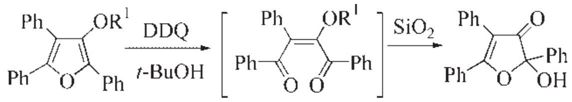
[a] **I**: 0.1 mmol; DDQ: 0.1 mmol; temp.: room temperature; alcohol (R^2OH): 6 mL.

In contrast, *cis*-1,4-diphenyl-2-ethoxy-2-butene-1,4-dione (**5**) was obtained with DDQ in *t*-BuOH (run 4). To clarify the particular solvent effect of *t*-BuOH in alcohols, various 3-alkoxyfurans were oxidized under the same reaction conditions. 3-Methoxy-, 3-propoxy-, 3-isopropoxy-, 3-butoxy-, and 3-isobutoxyfurans were also converted to corresponding 2-alkoxyenediones (**7**, **8**, **10**, **12**, and **14**) in 92–95% yields in *t*-BuOH (runs 5–9). Consequently, the oxidation of 3-alkoxy-2,5-diphenylfurans with DDQ in *t*-BuOH was confirmed to give 2-alkoxy-2-butene-1,4-diones chemoselectively.[20]

The oxidation of various 3-alkoxy-2,4,5-triphenylfurans was also carried out to clarify oxidizing power of DDQ in *t*-BuOH under the same reaction conditions. The results are shown in Table 2. The oxidation of 3-ethoxy-2,4,5-triphenylfuran (**16**) was examined with DDQ. 2-Ethoxy-1,3,4-triphenyl-2-butene-1,4-dione (**17**) was mainly obtained as crude product (run 1). 2-Ethoxy-1,3,4-triphenyl-2-butene-1,4-dione (**17**) spontaneously transformed to 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15**) during the purification of crude product by silica-gel column chromatography (run 1).

To examine the generation of 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15**) on this reaction system, the ring opening of various 3-alkoxy-2,4,5-triphenylfurans (**18**, **20**, **22**, and **24**) to 2-alkoxy-2-butene-1,4-diones was carried out with DDQ under the same reaction conditions. The oxidation of 3-alkoxy-2,4,5-triphenylfurans (**18**, **22**) afforded the respective *cis*-2-alkoxy-1,3,4-triphenyl-2-butene-1,4-diones (**19**, **23**) as crude product (runs 2, 4). The oxidation of branched alkoxyfurans (**20**, **24**) also took place to give the corresponding *cis*-2-alkoxyenediones (**21**, **25**) (runs 3, 5). Similarly, *cis*-2-

Table 2. Reaction of 3-alkoxyfurans with DDQ in *t*-BuOH[a]



IV **V** **15**

Run	IV	R¹	Time/(h)	Products, yield V[b]	 (%)	 15 (%)[b]
1	**16**	C_2H_5	14	**17**	92	91
2	**18**	C_3H_7	19	**19**	84	81
3	**20**	i-C_3H_7	20	**21**	90	87
4	**22**	C_4H_9	20	**23**	85	84
5	**24**	i-C_4H_9	15	**25**	90	89

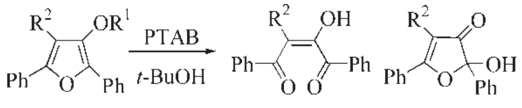
[a] **IV**: 0.1 mmol; DDQ: 01 mmol; temp.: room temperature; *t*-BuOH: 6 mL.

[b] Yield of **V** was determined with ^{1}H NMR, ^{13}C NMR of crude product. Alkoxyenediones **V** were not isolated after purification. Alkoxyenediones **V** were easily transformed to hydroxyfuranone **15** during purification by column chromatography over SiO_2.

alkoxyenediones (**19**, **21**, **23**, and **25**) were easily transformed to 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15**) after purification by silica-gel column chromatography. In the present experiments, the oxidative ring opening of 3-alkoxy-2,4,5-triphenylfurans with DDQ in *t*-BuOH was ascertained to afford 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15**) by the path, giving *cis*-2-alkoxyenediones as intermediate.

On the other hand, the oxidation of various 3-alkoxy-2,5-diphenyl- and 3-alkoxy-2,4,5-triphenylfurans with PTAB in alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and isobutyl alcohol was also reported to easily convert them to respective 2-alkoxy-3(2*H*)-furanones.[20b] Therefore, the oxidation of alkoxyfurans with PTAB in *t*-BuOH was carried out to compare with those of DDQ and PTAB in other alcohols. The results are summarized in Table 3. Treating 2,5-diphenyl-3-methoxyfurans (**6**) with an equivalent molar of PTAB over methoxyfuran (**6**) in *t*-BuOH, 1,4-diphenyl-2-hydroxy-2-butene-1,4-dione (**26**) was obtained (run 1). 2-Methoxyenedione (**7**), 2-*t*-butoxyenedione, and 2-*t*-butoxy-3(2*H*)-furanone were not afforded. To test the solvent effect of *t*-BuOH for the transformation of alkoxy-(L152), furan (L153) to hydroxyenedione with PTAB, the ring opening reaction of various 3-alkoxyfurans (**1**, **4**, **9**, **11**, **13**) was carried out in *t*-BuOH. Hydroxyenedione (**26**) was afforded in good yields (runs 2–6). The system PTAB in *t*-BuOH was ascertained to give 2-hydroxy-2-butene-1,4-diones easily. These results suggested that the system PTAB in *t*-BuOH was an alternative and efficient method for the cleavage of ethers to alcohols.[8b]

Table 3. Reaction of 3-alkoxyfurans with PTAB in *t*-BuOH[a]



VI **26**: R^2=H **15**: R^2=Ph

Run	VI	R^1	R^2	Time/(h)	Products, yield (%)	
1	**6**	CH_3	H	13	**26**	80
2	**1**	C_2H_5	H	18	**26**	83
3	**4**	C_3H_7	H	19	**26**	92
4	**9**	i-C_3H_7	H	24	**26**	80
5	**11**	C_4H_9	H	13	**26**	90
6	**13**	i-C_4H_9	H	15	**26**	83
7	**16**	C_2H_5	Ph	21	**15**	84
8	**22**	C_4H_9	Ph	20	**15**	83
9	**24**	i-C_4H_9	Ph	20	**15**	85

[a]**VI**: 0.1 mmol; PTAB: 0.1 mmol; temp.: room temperature; *t*-BuOH: 6 mL.

Further, the reaction of 3-alkoxy-2,4,5-triphenylfurans (**16**, **22**, and **24**) with PTAB in *t*-BuOH under the same reaction conditions was carried out to clarify the limitations and chemoselectivity for the transformation of alkoxyfurans to hydroxyenediones. Alkoxyfurans (**16**, **22**, and **24**) were smoothly converted to 2-hydroxy-2,4,5-triphenyl furanone (**15**) (runs 7–9). Both 2-*t*-butoxy-3(2*H*)-furanone and alkoxyenediones (**17**, **23**, **25**) generated in Table 2 were not observed with PTAB in *t*-BuOH. The oxidation of 3-alkoxy-2,4,5-triphenylfurans with PTAB was favorable and more easily gave 2-hydroxy-3(2*H*)-furanone (**15**) in comparison with that of DDQ.

In addition, 3-chloro- and 3-bromo-2,5-diphenylfurans were recovered unchanged with DDQ or PTAB in *t*-BuOH. 3-Chloro- and 3-bromo-2,4,5-triphenylfurans were also recoverd unchanged. 2,5-Diphenyl-3-propionylfuran was recovered unchanged under the same reaction conditions. 2-Methoxyfuran gave no corresponding enediones with DDQ. 4-(2-Furoyl)-2-butanone and 3-(2-furoyl)propanenitrile were also recovered unchanged with DDQ. Similarly, furil, 4-(2-furoyl)-2-butanone, and 3-(2-Furoyl)propanenitrile were not converted to corresponding furanones with PTAB. Furfuryl benzoate did not give corresponding enediones with PTAB. In the present experiments, 3-alkoxy substituents were required for the transformation of furans with DDQ or PTAB in *t*-BuOH to 2-hydroxy-2-butene-1,4-diones. As mentioned previously, 3-alkoxy substituents were also considered to play an important role in the direct transformation of 3-alkoxy-2,4,5-triphenylfurans to 2-hydroxy-3(2*H*)-furanone with PTAB in *t*-BuOH.[20]

In conclusion, the oxidation system DDQ in *t*-BuOH was confirmed to be an alternative convenient method for the transformation of 3-alkoxy-2,4,5-triphenylfurans to 2-alkoxy-2-butene-1,4-diones chemoselectively. 2-Alkoxy-1,3,4,-triphenyl-2-butene-1,4-diones were found to be spontaneously transformed to 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone by silica gel. On the contrary, the system PTAB in *t*-BuOH was established to be useful for the transformation of 3-alkoxy-2,5-diphenylfurans to 2-hydroxy-2-butene-1,4-diones. The system PTAB in *t*-BuOH was also found to be more effective for the direct conversion of 3-alkoxy-2,4,5-triphenylfurans to 2-hydroxy-2,4,5-triphenyl-3(2*H*)-furanone than DDQ.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX270 spectometer, and the chemical shifts are given relative to the internal $SiMe_4$ standard. MS spectra were run on a Bruker Daltonics-Apex III. Analyses were run on a Yanagimoto MT-6.

Typical Procedure for the Transformation of 3-Ethoxy-2,4,5-triphenylfuran (16) to 2-Ethoxy-1,3,4-triphenyl-2-butene-1,4-dione (17) with DDQ

To a solution of 3-ethoxy-2,4,5-triphenylfuran (**16**, 34 mg, 0.1 mmol) in *t*-butyl alcohol (6 mL) at rt, DDQ (23 mg, 0.1 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl after stirring for 14 h at rt and extracted with ethyl acetate. The organic layer was washed with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl and dried by $MgSO_4$. After removal of solvent in vacuo, the ^{1}H and ^{13}C NMR spectra of slightly soluble crude products were recorded in $CDCl_3$. 2-Ethoxy-1,3,4-triphenyl-2-butene-1,4-dione (**17**) was obtained (ca. 92% by NMR). The crude products were purified by column chromatography on silica gel (Wako C-200) with CCl_4 and CCl_4-$CHCl_3$ (3:2, v/v). 2-Hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15,** 32 mg, 0.091 mmol) was obtained in 91% yield.

Data

Compound **17**: ^{1}H NMR ($CDCl_3$) δ 1.22 (3H, t, $J = 7.2$Hz), 3.88 (2H, q, $J = 7.2$ Hz), 7.20–8.03 (15H, m). ^{13}C NMR ($CDCl_3$) δ 15.09, 67.24, 125.75, 127.83, 127.96, 128.03, 128.35, 128.55, 128.66, 129.16, 129.63, 132.34, 132.63, 133.96, 136.02, 137.53, 156.44, 192.68, 194.98.

Compound **15**: mp 192°C. IR (KBr, cm^{-1}) 3244, 3060, 1689, 1613, 1590, 1568, 1501, 1483, 1447, 1394, 1314, 1241, 1220, 1157, 1110, 1072, 1028, 1001, 969, 957, 908, 795, 779, 756, 731. ^{1}H NMR ($CDCl_3$) δ 7.25–7.77 (15H, m). ^{13}C NMR ($CDCl_3$) δ 102.04, 112.13, 125.06, 126.90, 127.60, 127.79, 128.33, 128.82, 129.21, 131.55, 136.02, 177.82, 198.36. HR-ESI-MS$[M + Na]^+$ m/z 351.0992 (calcd. 351.0997 for $C_{22}H_{16}O_3Na$).

Preparative Scale of Oxidation of 3-Butoxy-2,5-diphenylfuran (11) with DDQ in *t*-BuOH

To a solution of 3-butoxy-2,5-diphenylfuran (**11**, 292 mg, 1.0 mmol) in *t*-butyl alcohol (10 mL) at rt, DDQ (227 mg, 1.0 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl after stirring for 17 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl and dried by $MgSO_4$. After removal of solvent in vacuo, the ^{1}H and ^{13}C NMR spectra of crude products were recorded. 2-Butoxy-1,4-diphenyl-2-butene-1,4-dione (**12**) was obtained. The crude products were purified by column chromatography on silica gel (Wako C-200) with CCl_4 and $CHCl_3$ (3:2, v/v). 2-Butoxy-1,4-diphenyl-2-butene-1,4-dione (**12**, 280 mg, 0.91 mmol) was obtained in 91% yield.

Compound **19**: IR (neat, cm^{-1}) 1660. ^1H NMR ($CDCl_3$) δ 0.82 (3H, t, $J = 6.7$ Hz), 1.60 (2H, sext, $J = 6.7$ Hz), 3.76 (2H, t, $J = 6.7$ Hz), 7.19–8.03 (15H, m). ^{13}C NMR ($CDCl_3$) δ 10.17, 22.87, 72.92, 125.75, 127.78, 127.88, 128.01, 128.30, 128.57, 128.67, 128.73, 129.14, 129.23, 129.61, 129.72, 132.29, 132.56, 133.65, 136.02, 137.57, 156.89, 192.72, 194.94.

Compound **21**: IR (neat, cm^{-1}) 1660. ^1H NMR ($CDCl_3$) δ 1.22 (6H, d, $J = 6.0$ Hz), 4.15 (1H, sept, $J = 6.0$ Hz), 7.21–8.04 (15H, m). ^{13}C NMR ($CDCl_3$) δ 22.53, 74.41, 126.11, 127.81, 128.05, 128.28, 128.64, 128.71, 129.20, 129.65, 132.36, 133.63, 133.98, 136.08, 137.61, 155.66, 192.97, 195.21.

Compound **23**: IR (neat, cm^{-1}) 1672. ^1H NMR ($CDCl_3$) δ 0.79 (3H, t, $J = 7.2$ Hz), 1.23 (2H, m), 1.56 (2H, m), 3.80 (2H, t, $J = 6.7$ Hz), 7.19–8.03 (15H, m). ^{13}C NMR ($CDCl_3$) δ 13.49, 18.72, 31.50, 71.10, 125.75, 128.01, 128.30, 128.55, 128.66, 128.73, 129.12, 129.61, 129.68, 132.29, 133.63, 133.99, 136.04, 137.59, 156.85, 192.73, 194.94.

Compound **25**: ^1H NMR ($CDCl_3$) δ 0.80 (6H, d, $J = 6.4$ Hz), 1.86 (1H, m), 3.57 (2H, d, $J = 6.2$ Hz), 7.18–8.02 (15H, m). ^{13}C NMR ($CDCl_3$) δ 18.87, 26.64, 77.44, 125.75, 127.85, 127.92, 127.99, 128.23, 128.57, 128.67, 129.11, 129.59, 129.79, 132.25, 133.65, 133.98, 136.04, 137.62, 157.14, 192.72, 194.89.

Typical Procedure for the Transformation of 2,5-Diphenyl-3-isobutoxyfuran (13) to 1,4-Diphenyl-2-hydroxy-2-butene-1,4-dione (26) with PTAB

To a solution of 2,5-diphenyl-3-isobutoxyfuran (**13**, 29 mg, 0.1 mmol) in *t*-butyl alcohol (10 mL) at rt, PTAB (38 mg, 0.1 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl after stirring for 15 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl and dried by $MgSO_4$. After removal of solvent in vacuo, the ^1H and ^{13}C NMR spectra of crude products were recorded. 1,4-Diphenyl-2-hydroxy-2-butene-1,4-dione (**26**) were obtained. The crude products were purified by column chromatography on silica gel (Wako C-200) with CCl_4 and $CHCl_3$ (3:2, v/v). 1,4-Diphenyl-2-hydroxy-2-butene-1,4-dione (**26**, 21 mg, 0.83 mmol) was obtained in 83% yield.

Data

Compound **26**: IR (neat, cm^{-1}) 3381, 3065, 2926, 1681, 1600, 1566, 1490, 1449, 1358, 1320, 1267, 1181, 1144, 1100, 1076, 1053, 1026, 1001, 970, 899, 872, 832, 809, 774, 735. ^{1}H NMR ($CDCl_3$) δ 6.85 (1H, s), 7.25–8.14 (10H, m). ^{13}C NMR ($CDCl_3$) δ 96.20, 127.56, 128.62, 128.78, 128.84, 130.45, 133.44, 133.67, 134.21, 182.29, 187.04, 190.45. Anal. calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.31; H, 4.92. HR-ESI-MS$[M + Na]^+$ m/z 275.0678 (calcd. 275.0679 for $C_{16}H_{12}O_3Na$).

Preparative Scale of Oxidation of 3-Butoxy-2,4-diphenylfuran (11) with PTAB in *t*-BuOH

To a solution of 3-butoxy-2,5-diphenylfuran (**11**, 292 mg, 1.0 mmol) in *t*-butyl alcohol (10 mL) at rt, PTAB (376 mg, 1.0 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl after stirring for 17 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl and dried by $MgSO_4$. After removal of solvent in vacuo, the ^{1}H and ^{13}C NMR spectra of crude products were recorded. 1,4-Diphenyl-2-hydroxy-2-butene-1,4-dione (**26**) was obtained. The crude products were purified by column chromatography on silica gel (Wako C-200) with CCl_4 and $CHCl_3$ (3:2, v/v). 1,4-Diphenyl-2-hydroxy-2-butene-1,4-dione (**26,** 222 mg, 0.88 mmol) was obtained in 88% yield.

Typical Procedure for the Transformation of 3-Isobutoxy-2,4,5-triphenylfuran (24) to 2-Hydroxy-2,4,5-triphenyl-3 (2*H*)-(L340), furanone (L341) with PTAB

To a solution of 3-isobutoxy-2,4,5-triphenylfuran (**24,** 36 mg, 0.1 mmol) in *t*-butyl alcohol (6 mL) at rt, PTAB (38 mg, 0.1 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl after stirring for 20 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and saturated aq NaCl and dried by $MgSO_4$. After removal of solvent in vacuo, the ^{1}H and ^{13}C NMR spectra of slightly soluble crude products were recorded in $CDCl_3$. 2-Hydroxy-2,4,5-triphenyl-3 (2*H*)-furanone (**15**) was obtained. The crude products were purified by column chromatography on silica gel (Wako C-200) with CCl_4-$CHCl_3$ (3:2, v/v). 2-Hydroxy-2,4,5-triphenyl-3(2*H*)-furanone (**15,** 30 mg, 0.85 mmol) was obtained in 85% yield.

REFERENCES

1. (a) Larock, R. C. *In Comprehensive Organic Transformations*, 2nd Edn.; Wiley-VCH: New York, 1999, p.1260; (b) Ho, T.-L. *Fiesers' Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1967–2003, Vol. 1–21.

2. (a) Oh, H.; Lee, S.; Lee, H.-S.; Lee, D.-H.; Lee, S. Y.; Chung, H.-T.; Kim, T. S.; Kwon, T.-O. *Phytochemistry.* **2002**, *61*, 175; (b) Li, C.; Gloer, J. B.; Wicklow, D. T.; Dowd, P. F. *Org. Lett.* **2002**, *4*, 3095; (c) Look, S. A.; Burch, M. T.; Fenical, W.; Qi-tai, Z.; Clardy, J. *J. Org. Chem.* **1985**, *50*, 5741; (d) Clive, D. L. J.; Minaruzzaman; Ou, L. *J. Org. Chem.* **2005**, *70*, 3318.
3. Cimino, G.; Sodano, G.; Spinella, A. *J. Org. Chem.* **1987**, *52*, 5326.
4. (a) Hayakawa, Y.; Kawakami, K.; Seto, H.; Furihata, K. *Tetrahedron Lett.* **1992**, *33*, 2701; (b) Harrington, P. E.; Tius, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 8509; (c) Dyke, C. A.; Bryson, T. A. *Tetrahedron Lett.* **2004**, *45*, 6051; (d) Boger, D. L.; Hong, J. *J. Am. Chem. Soc.* **2001**, *123*, 8515; (e) Tse, B.; Jones, A. B. *Tetrahedron Lett.* **2001**, *42*, 6429.
5. (a) D'Ambrosio, M.; Fabbri, D.; Guerriero, A.; Pietra, F. *Helv. Chim. Acta* **1987**, *70*, 63; (b) Williams, D.; Andersen, R. J.; Duyne, G. D. V.; Clardy, J. *J. Org. Chem.* **1987**, *52*, 332.
6. (a) Gunn, B. P. *Tetrahedron Lett.* **1985**, *26*, 2869; (b) Jurczak, J.; Pikul, S. *Tetrahedron Lett.* **1985**, *26*, 3039.
7. Williams, P. D.; LeGoff, E. *J. Org. Chem.* **1981**, *46*, 4143.
8. (a) Mondal, E.; Barua, P. M. B.; Bose, G.; Khan, A. T. *Chem. Lett.* **2002**, 210; (b) Gopinath, R.; Patel, B. K. *Org. Lett.* **2000**, *2*, 4177.
9. (a) Smith, A. B., III; Guaciaro, M. A.; Schow, S. R.; Wovkulich, P. M.; Toder, B. H.; Hall, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 219; (b) Caine, D. S.; Arant, M. E. *Synlett* **2004**, 2081; (c) Winkler, J. D.; Oh, K.; Asselin, S. M. *Org. Lett.* **2005**, *7*, 387; (d) Liu, Y.; Liu, M.; Guo, S.; Tu, H.; Zhou, Y.; Gao, H. *Org. Lett.* **2006**, *8*, 3445.
10. (a) Tanis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1983**, *48*, 4572; (b) D'Annibale, A.; Scettri, A. *Tetrahedron Lett.* **1995**, *36*, 4659; (c) Ballini, R.; Barboni, L.; Bosica, G.; Petrini, M. *Synlett* **2000**, 391; (d) Gopalakrishnan, G.; Pradeep Singh, N. D.; Kasinath, V.; Siva Rama Krishnan, M.; Malathi, R.; Rajan, S. S. *Tetrahedron Lett.* **2001**, *42*, 6577; (e) Surya Prakash Rao, H.; Jothilingam, S. *Tetrahedron Lett.* **2001**, *42*, 6595.
11. Antonioletti, R.; D'Auria, M.; Piancatelli, G.; Scettri, A. *J. Chem. Soc., Perkin. Trans.1* **1981**, 2398.
12. Kobayashi, Y.; Katsuno, H.; Sato, F. *Chem. Lett.* **1983**, 1771.
13. Williams, P. D.; LeGoff, E. *Tetrahedron Lett.* **1985**, *26*, 1367.
14. Gingerich, S. B.; Jennings, P. W. *J. Org. Chem.* **1984**, *49*, 1284.
15. Dominguez, C.; Csaky, A. G.; Plumet, J. *Tetrahedron Lett.* **1990**, *31*, 7669.
16. Adger, B. M.; Barrett, C.; Brennan, J.; McKervey, M. A.; Murray, R. W. *J. Chem. Soc., Chem. Commun.* **1991**, 1553.
17. Finlay, J.; McKervey, M. A.; Nimal-Gunaratne, H. Q. *Tetrahedron Lett.* **1998**, *39*, 5651.
18. Massa, A.; Acocella, M. R.; Rosa, M. D.; Soriente, A.; Villano, R.; Scettri, A. *Tetrahedron Lett.* **2003**, *44*, 835.
19. (a) Sayama, S.; Onami, T. *Synlett* **2004**, 2369; (b) Sayama, S.; Onami, T. *Synlett* **2004**, 2739; (c) Sayama, S. *Synlett* **2006**, 1479; (d) Sayama, S. *Tetrahedron Lett.* **2006**, *47*, 4001.
20. (a) Sayama, S.; Inamura, Y. *Heterocycles* **1996**, *43*, 1371; (b) Sayama, S. *Heterocycles* **2005**, *65*, 1347.