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CONVENIENT TRANSFORMATION OF 3-ALKOXYFURANS TO 2-ALKOXY-3-FURANONES OR *cis*-2-ALKOXY-2-BUTENE-1,4-DIONES WITH PHENYLTRIMETHYLAMMONIUM TRIBROMIDE

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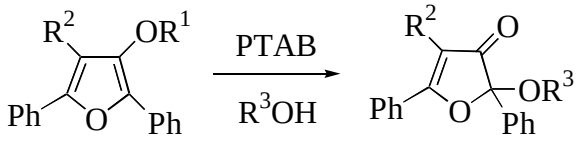
Abstract – 3-Alkoxy-2,5-diphenylfurans and 3-alkoxy-2,4,5-triphenylfurans were converted to 2-alkoxy-3-furanones with phenyltrimethylammonium tribromides(PTAB) in various alcohols at room temperature. The oxidative ring-opening of 3-alkoxy-2,5-diphenylfurans to *cis*-2-alkoxy-2-butene-1,4-diones was also accomplished with PTAB in DMSO.

Novel antibiotics, antitumors, and antiinsection such as roseophilin, jatrophone, eremantholide, geiparvarine, and thiersinine possess 3-furanone, 2-butene-1,4-dione, and 3-alkoxyfuran moieties, respectively.[1-6] Therefore, synthetic methods for the 3-furanone, 3-alkoxyfuran, and 2-alkoxy-2-butene-1,4-dione skeletons have been developed.[7, 10-14] On the other hand, furan derivatives have been used as precursors in the synthesis of natural products because of their latent enedicarbonyl functionality and butyrolactone moiety. The classical approach to oxidative ring-opening of furans involves, first, the preparation of the α,α-dimethoxydihydrofuran derivatives by treating the furans with Br_2 in buffered methyl alcohol and then hydrolysis to enediones.[1a,7] However, enediones and furans have been known to isomerize to *tetra*-ring-opened *bis*(*trans*-enedione) or resinous substances under acidic conditions.[7c] Therefore, it is significant to explore a convenient and regioselective transformation of furans into enediones or furanones in organic synthesis. Since ammonium tribromides such as phenyltrimethylammonium tribromide (PTAB) and pyridinium hydrobromide perbromide(PHPB) are much easier to handle and maintain the desired stoichiometry in comparison with Br_2, the use of commercially available PTAB and PHPB has been more advantageous and attractive than that of Br_2.[1b, 8] PTAB was also reported to be an available and chemoselective reagent for oxidation of secondary alcohols and 1,2-diols to the corresponding ketones, 1,2-diketones, and α-hydroxy ketones in the presence of catalytic amounts of $SbBr_3$ or $CuBr_2$ in the previous paper.[9a] We considered it interesting to

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



S **a**

Run	**S**	R^1	R^2	Alcohol[b] / R^3	Time (h)		Yield (%)
1	**1**	C_4H_9	H	CH_3	70	**1a**	66
2	**1**	C_4H_9	H	C_2H_5	20	**2a**	86
3	**1**	C_4H_9	H	*i*-C_3H_7	41	**3a**	85
4	**1**	C_4H_9	H	*i*-C_4H_9	20	**4a**	92
5	**2**	C_2H_5	H	*i*-C_4H_9	20	**4a**	94
6	**3**	C_2H_5	Ph	C_2H_5	48	**5a**	93
7	**3**	C_2H_5	Ph	*i*-C_3H_7	75	**6a**	68
8	**4**	C_4H_9	Ph	C_2H_5	48	**5a**	83
9	**4**	C_4H_9	Ph	*i*-C_3H_7	48	**6a**	57
10	**5**	*i*-C_4H_9	Ph	C_2H_5	24	**5a**	88
11	**3**	C_2H_5	Ph	C_2H_5	43	**5a**	88[c]
12	**3**	C_2H_5	Ph	*i*-C_3H_7	24	**6a**	63[c]
13	**3**	C_2H_5	Ph	*i*-C_4H_9	43	**7a**	88[c]

[a] **1**: 0.1 mmol; PTAB: 0.1 mmol; Temp: Room temperature.
[b] Solvent: R^3OH, 6 mL [c] PHPB(0.1 mmol) was used instead of PTAB.

find a new procedure for regioselective transformation of alkoxyfurans to alkoxyfuranones or alkoxyenediones with ammonium tribromides instead of Br_2 and other oxidative reagents. We would like to report the results of our studies concerning the transformation of 3-alkoxyfurans to alkoxyfuranones and alkoxyenediones with PTAB or PHPB.[9a] As furanones have been known to affect germination and growth as metabolites in phytochemistry, the effective methods for the synthesis of 3-furanone derivatives has been investigated.[10] On the other hand, simple and regioselective transformation of 3-alkoxyfurans to 3-furanone derivatives has been little studied in comparison with the

oxidative conversion of furans to enediones or lactones.[7, 11-14]

Therefore, the transformation of 3-alkoxyfurans to 3-furanone derivatives was carried out with PTAB in various solvents. At first, the reaction of 3-butoxy-2,5-diphenylfuran (**1**), chosen as a representative 3-alkoxyfuran for this study, was carried out with PTAB in various alcohols at room temperature. The results are summarized in Table 1. At a 1 : 1 molar ratio of **1** and PTAB, 2-methoxy-3-furanone(**1a**) was mainly obtained in methyl alcohol(Run 1). To exhibit the solvent effect of alcohol, the transformation of **1** was carried out with PTAB in various alcohols. Butoxyfuran (**1**) was also converted to 2,5-diphenyl-2-ethoxy-3-furanone(**2a**) in ethyl alcohol under the same reaction conditions(Run 2). Butoxyfuran (**1**) was easily transformed to 2-alkoxy-3-furanoes(**3a**-**4a**) with PTAB in isopropyl alcohol, isobutyl alcohol, respectively(Runs 3, 4). 3-Ethoxyfuran (**2**) was similarly converted to 2-isobutoxy-3-furanone (**4a**) in isobutyl alcohol (Run 5). Thus, the 3-alkoxyfuranes turned out to be converted to 2-alkoxyfuranones in various alcohols easily.

Tetra-substituted alkoxyfurans were also examined to clarify the limitations and regioselectivity for the transformation of 3-alkoxyfurans to 2-alkoxy-3-furanones in various alcohols. 3-Ethoxy-2,4,5-triphenylfuran(**3**) was similarly converted to 2-ethoxy-2,4,5-triphenyl-3-furanone(**5a**) in ethyl alcohol under the same reaction conditions(Run 6), while the yield of 2-isopropoxy-3-furanone(**6a**) was not fully satisfactory in isopropyl alcohol(**6a**: 68%, Run 7).[15]

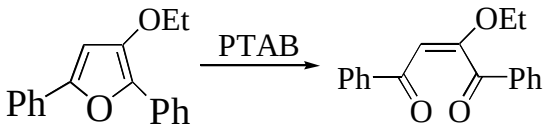
To examine the effect of PTAB in alcohol, the transformation of ethoxyfuran (**3**) was carried out with Bu_4NBr and KBr in propyl alcohol. Ethoxyfuran (**3**) was recovered unchanged in over 94% yield even for prolonged reaction times(70-75 h), respectively. Ethoxyfuran (**3**) was also recovered unchanged in 95% yield without PTAB in propyl alcohol. At the 1 : 0.3 molar ratio of ethoxyfuran (**3**) and PTAB in ethanol, 2-ethoxy-3-furanone (**5a**) was obtained only in 35% yield accompanied by unchanged **3** (47%) after 40 h at room temperature. In the present experiments, an equal or excess molar equivalent of PTAB over 3-alkoxyfuran in alcohol was essential for obtaining 2-alkoxy-3-furanones in good yields. 3-Butoxy-2,4,5-triphenylfuran (**4**) was also transformed to 2-ethoxy-3-furanone (**5a**) with PTAB in good yield in ethyl alcohol (Run 8). On the contrary, reaction in isopropyl alcohol produced 2-isopropoxy-3-furanone (**6a)** in 57% yield (Run 9).[15] 3-Isobutoxy-2,4,5-triphenylfuran(**5**) was similarly converted to the corresponding 2-ethoxy-3-furanones (**5a**) in ethyl alcohol(Run 10). The transformation of tetrasubstituted alkoxyfurans to alkoxyfuranones with PHPB was also carried out to compare the reactivity between ammmonium tribromides PTAB and PHPB. Ethoxyfuran (**3**) was also found to be converted to the corresponding 2-alkoxy-3-furanones(**5a**, **7a**) in good yields with PHPB in ethyl alcohol, and in isobutyl alcohol(Runs 11, 13). The yield of 2-isopropoxy-3-furanone (**9a**) was not fully satisfactory even with PHPB, either Run 7 (63 %, Run 12).[15] As mentioned above, ammonium tribromides PTAB and PHPB were ascertained to be simple and regioselective for the transformation of

3-alkoxyfurans to 2-alkoxy-3-furanones in various alcohols.

On the other hand, the ring-opening of furans to enediones has been performed with many reagents instead of Br_2. The conversion of furans to enediones was achieved by using oxidative reagents such as pyridinium chlorochromate (PCC), *m*-chloroperbenzoic acid (*m*CPBA), magnesium monoperoxy-phthalate, dioxirane, methyltrioxorhenium/urea hydrogen peroxide.[12-14] Further, a simple and convenient procedure for conversion of furans to *cis*- and *trans*-enediones was also reported using $Mo(CO)_6$/cumyl hydroperoxide.[14g] We subsequently considered it interesting to examine other utility of ammmonium tribromides PTAB, PHPB and to find a new procedure for selective oxidation of 3-alkoxyfurans to alkoxyenediones. We would also like to report the results of our studies concerning the oxidation of 3-alkoxyfurans to endiones with PTAB. The oxidation of 2,5-diphenyl-3-ethoxyfuran (**2**), chosen as a representative alkoxyfuran for this study, was carried out with PTAB in various solvents at room temperature. The results are summarized in Table 2. *cis*-Ethoxyenedione (**2b**) was not afforded in good yield at the 2.0 molar equivalents of PTAB over **2** in THF (Run 1). Therefore, the use of another solvent was needed for obtaining *cis*-ethoxyenedione (**2b**) in moderate yield. In THF-DMSO(v/v, 2 : 1), ethoxyenedione (**2b**) was mainly obtained at the 1 : 2 molar ratio of **2** and PTAB(Run 2). Ethoxyfuran (**2**) was also oxidized to give *cis*-ethoxyenedione (**2b**) in good yield in THF-DMSO even at the 1 : 1 molar ratio of **2** and PTAB (Run 3). Further, ethoxyfuran (**2**) took place to give a complex mixture of enedione and furanone accompanied by **2** in CH_2Cl_2 or DME. Consequently, DMSO was found to be an effective solvent for the ring-opening of alkoxyfurans to alkoxyenediones with PTAB at room temperature. The reaction of **2** was also carried out to examine the effect of the bromide ion for the ring-opening of ethoxyfuran (**2**) to enedione (**2b**) with Bu_4NBr or KBr in DMSO, respectively. Ethoxyfuran (**2**) was recovered unchanged in over 90 % yields. PTAB was ascertained to be essential for the ring-opening of alkoxyfurans to alkoxyenediones. Further, at 0.7 molar equivalents of PTAB over **2,** ethoxyenedione **2b** was not obtained in high yield accompanied by **2** (Run 4). At 1.0 molar equivalents of PTAB in DMSO, ethoxyfuran (**2**) was converted to *cis*-ethoxyenedione (**2b**) in good yield(Run 5). The optimum conditions for obtaining *cis*-alkoxyenediones found in the present experiments, are needed to use an equal molar equivalent of PTAB over alkoxyfuran and to use DMSO as a solvent.

The oxidation of various 3-alkoxy-2,5-diphenylfurans was carried out to clarify the the oxidizing power of PTAB in THF-DMSO or DMSO, respectively. The results are shown in Table 3. The oxidation of 3-alkoxyfurans(**1**, **6**, **7**) with PTAB in THF-DMSO, afforded the respective *cis*-2-alkoxyenediones (**1b, 6b, 7b**) in good yields without producing resinous substances(Runs 1-3). The oxidation of branched 3-alkoxyfurans (**8**, **9**) also took place to give the corresponding *cis*-2-alkoxyenediones (**8b**, **9b**)(Runs 4, 5).

Table 2 Oxidation of 2,5-diphnyl-3-ethoxyfuran (**2**) with PTAB[a]

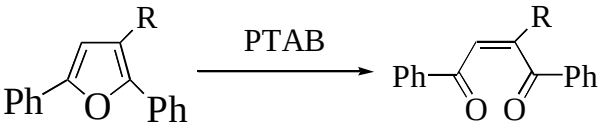


2 **2b**

Run	Molar ratio / **2** / PTAB	Solv [b]	Time (h)	Yield (%)	
				2b	**2**
1	2.0	A	17	35	33
2	2.0	B	16	88	--
3	1.0	B	24	83	--
4	0.7	B	28	57	26
5	1.0	C	24	89	--

[a] **2**: 0.5 mmol; Temp: Room temperature. [b] Solvent: 15 mL; A=THF; B=THF-DMSO(2:1, v/v). C=DMSO.

Table 3 Oxidation of furans with PTAB[a]



S **b**

Run	**S**	R	Solvent[b]	Time (h)	Yield (%)	
1	**6**	CH_3O	B	22	**6b**	80
2	**7**	C_3H_7O	B	21	**7b**	82
3	**1**	C_4H_9O	B	17	**1b**	95
4	**8**	*i*-C_3H_7O	B	22	**8b**	95
5	**9**	*i*-C_4H_9O	B	31	**9b**	83
6	**1**	C_4H_9O	C	21	**1b**	96

Table 3 (*continued*)

Run	**S**	R	Solvent[b]	Time (h)	Yield (%)	
7	**9**	*i*-C_4H_9O	C	22	**9b**	96
8	**10**	H	C	27	Recovered	**10** 94
9	**11**	Ph	C	27	Recovered	**11** 90
10	**12**	$COCH_3$	C	93	Recovered	**12** 90

[a] **S**: 0.5 mmol; PTAB: 0.5 mmol. Temp: Room temperature.
[b] Solvent: 15 mL, B=THF-DMSO(2:1, v/v), C=DMSO.

In DMSO, alkoxyfurans (**1**, **9**) were converted to corresponding alkoxyenediones (**1b**, **9b**) in good yields(Runs 6, 7).

On the contrary, furans (**10**, **11**, **12)** were recovered unchanged with PTAB in DMSO (Runs 8-10). The oxidation system PTAB in DMSO was confirmed to be a chemoselective procedure for the oxidation of 3-alkoxyfurans to *cis*-alkoxyenediones as well as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) reported in the previous paper.[14h]

In conclusion, the systems PTAB or PHPB in various alcohols were found to be convenient methods for the transformation of 3-alkoxyfurans to 2-alkoxy-3-furanones. Further, the oxidation system PTAB in DMSO was also demonstrated to provide an alternative simple and chemoselective procedure for the oxidative ring-opening of 3-alkoxyfurans to *cis*-2-alkoxy-2-butene-1,4-diones.[16]

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 spectrometer and the chemical shifts are given relative to internal $SiMe_4$ standard. MS spectra were run on a Bruker Daltonics–APEX III.

A typical procedure is described for the transformation of 2,5-diphenyl-3-ethoxyfuran (2) to 2,5-diphenyl-2-isobutoxy-3(2*H*)-furanone (4a) with PTAB: To a solution of **2** (30 mg, 0.1 mmol) in isobutyl alcohol(6 mL) at rt, PTAB (38 mg, 0.1 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ 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 successively saturated aq NaCl and dried by $MgSO_4$. After removal of the solvent in vacuo, residual isobutyl alcohol was removed with CCl_4(20 mL x 2) in vacuo

two times. The residue was purified by column chromatography on silica gel(Wakogel C-200) with CCl_4 and $CHCl_3$ (3:2 v/v). 2-Isobutoxy-3-furanone (**4a**, 29 mg, 0.094 mmol) was obtained in 94 % yield.

A typical procedure is described for the transformation of 3-ethoxy-2,4,5-triphenylfuran (3) to 2-isobutoxy-2,4,5-triphenyl-3(2*H*)-furanone (7a) with PHPB: To a solution of **3** (34 mg, 0.1 mmol) in isobutyl alcohol(6 mL) at rt, PHPB (32 mg, 0.1 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ after stirring for 43 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and successively saturated aq NaCl and dried by $MgSO_4$. After removal of the solvent in vacuo, residual isobutyl alcohol was removed with CCl_4(20 mL x 2) in vacuo two times. The residue was purified by column chromatography on silica gel(Wakogel C-200) with CCl_4 and $CHCl_3$ (3:2 v/v). 2-Isobutoxy-3-furanone (**7a**, 34 mg, 0.088 mmol) was obtained in 88 % yield.

A typical procedure is described for the oxidation of 2,5-diphenyl-3-ethoxyfuran (2) to *cis*-1,4-diphenyl-2-ethoxy-2-butene-1,4-dione (2b): To a solution of **2**(132 mg, 0.5 mmol) in THF-DMSO(15 mL, v/v 2:1) at rt, PTAB (188 mg, 0.5 mmol) was added. The reaction mixture was treated with 0.5 M aq $Na_2S_2O_3$ after stirring for 24 h at rt and extracted with ethyl acetate. The organic layer was washed by 0.5 M aq $Na_2S_2O_3$ and successively saturated aq NaCl and dried by $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel(Wakogel C-200) with CCl_4 and $CHCl_3$ (1:1 v/v). *cis*-Ethoxyenedione (**2b**,116 mg, 0.41 mmol) was obtained in 83 % yield.

2,5-Diphenyl-2-methoxy-3(2*H*)-furanone (**1a**). mp 98-99 ^oC. IR(KBr, cm^{-1}) 3061, 2943, 2840, 1698, 1643, 1601, 1590, 1564, 1491, 1448, 1400, 1359, 1314, 1288, 1247, 1212, 1188, 1117, 1076, 1052, 1037, 958, 938, 921, 876, 856, 805, 778, 765, 732, 710. ^1H NMR($CDCl_3$) δ 3.49(3H, s), 6.06(1H, s), 7.36-7.99(10H, m). ^{13}C NMR($CDCl_3$) δ 52.77, 99.28, 107.36, 125.85, 127.33, 128.24, 128.53, 129.09, 129.48, 133.42, 134.41, 184.56, 199.02. *Anal*. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.69; H, 5.45.

2,5-Diphenyl-2-ethoxy-3(2*H*)-furanone (**2a**). mp 86-87 ^oC. IR(KBr, cm^{-1}) 3072, 2980, 2898, 1710, 1602, 1591, 1564, 1489, 1451, 1355, 1240, 1210, 1141, 1106, 1051, 984, 949, 873, 804, 777, 764, 737. ^1H NMR($CDCl_3$) δ 1.30(3H, t, *J*=7.0 Hz), 3.74(2H, q, *J*=7.0 Hz), 6.04(1H, s), 7.34-7.39(3H, m), 7.51-7.65(5H, m), 7.95-7.99(2H, m). ^{13}C NMR($CDCl_3$) δ 15.27, 61.27, 99.17, 107.49, 126.84, 127.33, 128.39, 128.49, 129.07, 129.38, 133.35, 134.87, 184.36, 199.26. *Anal*. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.20; H, 5.91.

2,5-Diphenyl-2-isopropoxy-3(2*H*)-furanone (**3a**). mp 150-151 °C. IR(KBr, cm^{-1}) 3107, 3060, 2971, 2927, 2870, 1709, 1602, 1565, 1489, 1462, 1447, 1380, 1369, 1352, 1315, 1299, 1236, 1211, 1178, 1134, 1108, 1077, 1052, 1026, 1000, 983, 963, 935, 919, 843, 797, 776, 765, 743, 710. ^{1}H NMR($CDCl_3$) δ 1.25(3H, d, *J*=5.9 Hz), 1.33(3H, d, *J*=5.9 Hz), 4.04(1H, sept, *J*=5.9 Hz), 6.04(1H, s), 7.33-7.38(3H, m), 7.51-7.69(5H, m), 7.94-7.98(2H, m). ^{13}C NMR($CDCl_3$) δ 23.88, 24.26, 70.40, 99.15, 108.17, 125.94, 127.26, 128.42, 128.57, 129.09, 129.29, 133.27, 135.29, 183.95, 199.26. *Anal*. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C,77.52; H, 6.30.

2,5-Diphenyl-2-isobutoxy-3(2*H*)-furanone (**4a**). IR(neat, cm^{-1}) 3105, 3064, 3034, 2958, 2930, 2874, 1709, 1604, 1592, 1566, 1490, 1469, 1449, 1395, 1355, 1298, 1237, 1212, 1180, 1126, 1077, 1052, 1038, 1026, 1000, 987, 965, 943, 871, 806, 777, 763, 740, 710. ^{1}H NMR($CDCl_3$) δ 0.96(3H, d, *J*=6.7 Hz), 0.94(3H, d, *J*=6.7 Hz), 1.95(1H, m), 3.43(2H, m), 6.05(1H, s), 7.34-7.63(8H, m), 7.95-7.99(2H, m). ^{13}C NMR($CDCl_3$) δ 19.22, 28.55, 71.78, 99.30, 107.42, 125.84, 127.34, 128.48, 129.09, 129.36, 133.35, 135.07, 184.40, 199.40. *Anal*. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.59; H, 6.70.

2-Ethoxy-2,4,5-triphenyl-3(2*H*)-furanone (**5a**). IR(neat, cm^{-1}) 3061, 2979, 2932, 2896, 1708, 1614, 1592, 1571, 1486, 1448, 1383, 1315, 1229, 1146, 1095, 1073, 1031, 986, 962, 910, 756. ^{1}H NMR($CDCl_3$) δ 1.32(3H, t, *J*=7.0 Hz), 3.79(2H, q, *J*=7.0 Hz), 7.27-7.81(15H, m). ^{13}C NMR($CDCl_3$) δ 15.34, 61.24, 105.58, 114.50, 126.11, 127.88, 128.32, 128.60, 128.66, 129.23, 129.30, 129.43, 129.56, 132.48, 135.00, 178.75, 198.31. HR-ESI-MS $[M+Na]^+$ m/z 379.1304 (Calcd 379.1305 for $C_{24}H_{20}O_3Na$).

2-Isopropoxy-2,4,5-triphenyl-3(2*H*)-furanone (**6a**). IR(neat, cm^{-1}) 3062, 3027, 2976, 2930, 1706, 1614, 1592, 1570, 1501, 1485, 1465, 1448, 1383, 1315, 1229, 1180, 1153, 1094, 1072, 1029, 1003, 991, 958, 932, 909, 842, 755, 715. ^{1}H NMR($CDCl_3$) δ 1.30(3H, d, *J*=6.2 Hz), 1.34(3H, d, *J*=6.2 Hz), 4.09(1H, sept, *J*=6.2 Hz), 7.24-7.82(15H, m). ^{13}C NMR($CDCl_3$) δ 23.99, 24.31, 70.31, 106.29, 114.50, 126.21, 127.85, 127.94, 128.49, 128.57, 128.62, 128.69, 129.34, 129.43, 129.61, 132.41, 135.47, 178.40, 198.31. HR-ESI-MS $[M+Na]^+$ m/z 393.1461 (Calcd 393.1461 for $C_{25}H_{22}O_3Na$).

2-Isobutoxy-2,4,5-triphenyl-3(2*H*)-furanone (**7a**). IR(neat, cm^{-1}) 3062, 3027, 2959, 2929, 2874, 1708, 1615, 1592, 1571, 1486, 1469, 1448, 1383, 1315, 1228, 1179, 1145, 1095, 1073, 1039, 1028, 1010, 961, 910, 756, 714. ^{1}H NMR($CDCl_3$) δ 0.97(3H, d, *J*=7.0 Hz), 0.98(3H, d, *J*=7.0 Hz), 1.99(1H, sept, *J*=7.0), 3.48(2H, m), 7.26-7.81(15H, m). ^{13}C NMR($CDCl_3$) δ 19.28, 28.59, 71.69, 105.48, 114.55, 126.07, 127.87, 128.49, 128.58, 129.23, 129.34, 129.56, 132.47, 135.18, 178.75, 198.36. HR-ESI-MS $[M+Na]^+$ m/z

407.1619 (Calcd 407.1618 for $C_{26}H_{24}O_3Na$).

***cis*-2-Butoxy-1,4-diphenyl-2-butene-1,4-dione** (**1b**). IR(neat, cm^{-1}) 3066, 2962, 2876, 1688, 1657, 1599, 1582, 1566, 1452, 1381, 1319, 1224, 1193, 1050, 1027, 1002, 982, 882, 864, 837, 783, 704. ^1H NMR($CDCl_3$) δ 0.94(3H, t, *J*=7.2 Hz), 1.44(2H, m), 1.81(2H, m), 4.14(2H, t, *J*=7.2), 6.52(1H, s), 7.38-7.59(6H, m), 7.87-7.98(4H, m). ^{13}C NMR($CDCl_3$) δ 13.58, 19.01, 30.42, 70.47, 98.04, 128.05, 128.26, 128.44, 128.67, 128.76, 132.66, 133.49, 134.48, 137.75, 169.09, 188.48, 191.26. *Anal*. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.58; H, 6.69.

***cis*-1,4-Diphenyl-2-ethoxy-2-butene-1,4-dione** (**2b)**. IR(KBr, cm^{-1}) 1688, 1642, 1597, 1580, 1549, 1473, 1454, 1396, 1323, 1226, 1195, 1158, 1058, 1023, 1000, 975, 897, 853, 789, 706. ^1H NMR($CDCl_3$) δ 1.45(3H, t, *J*=7.2 Hz), 4.21(2H, q, *J*=7.2 Hz), 6.52(1H, s), 7.38-7.59(6H, m), 7.86-7.98(4H, m). ^{13}C NMR($CDCl_3$) δ 14.07, 66.45, 98.09, 128.05, 128.46, 128.69, 128.80, 132.68, 133.51, 134.46, 137.77, 168.85, 188.46, 191.28. *Anal*. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C,77.21; H, 5.92.

***cis*-1,4-Diphenyl-2-methoxy-2-butene-1,4-dione** (**6b**). IR(neat, cm^{-1}) 3066, 3030, 2942, 1686, 1659, 1599, 1582, 1568, 1450, 1381, 1311, 1226, 1203, 1176, 1048, 1027, 1009, 949, 857, 826, 783, 704. ^1H NMR($CDCl_3$) δ 3.97(3H, s), 6.54(1H, s), 7.39-7.59(6H, m), 7.88-7.96(4H, m). ^{13}C NMR($CDCl_3$) δ 57.32, 97.91, 128.08, 128.48, 128.71, 128.80, 132.77, 133.62, 134.37, 137.64, 169.41, 188.37, 191.17. *Anal*. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.22; H, 5.13.

***cis*-1,4-Diphenyl-2-propoxy-2-butene-1,4-dione** (**7b**). IR(neat, cm^{-1}) 3066, 2974, 2942, 2882, 1688, 1659, 1599, 1582, 1566, 1452, 1381, 1313, 1226, 1193, 1052, 1027, 1002, 986, 942, 870, 783, 764, 704. ^1H NMR($CDCl_3$) δ 1.01(3H, t, *J*=7.2 Hz), 1.84(2H, m), 4.10(2H, t, *J*=6.3 Hz), 6.52(1H, s), 7.38-7.59(6H, m), 7.87-7.98(4H, m). ^{13}C NMR($CDCl_3$) δ 10.33, 21.88, 72.20, 98.09, 128.06, 128.46, 128.69, 128.80, 132.66, 133.51, 134.51, 137.79, 169.09, 188.48, 191.24. *Anal*. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C,77.29 ; H, 6.08.

***cis*-1,4-Diphenyl-2-isopropoxy-2-butene-1,4-dione** (**8b**). IR(KBr, cm^{-1}) 2980, 1686, 1638, 1597, 1578, 1545, 1454, 1392, 1315, 1226, 1197, 1158, 1102, 1056, 1027, 1000, 977, 936, 913, 872, 843, 795, 775, 712, 700. ^1H NMR($CDCl_3$) δ 1.46(6H, d, *J*=5.9 Hz), 4.74(1H, sept, *J*=5.9 Hz), 6.51(1H, s), 7.38-7.59(6H, m), 7.85-7.98(4H, m). ^{13}C NMR($CDCl_3$) δ 21.40, 73.87, 98.18, 128.04, 128.44, 128.69, 128.76, 132.61, 133.44, 134.50, 137.89, 167.96, 188.58, 191.26. *Anal*. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C,77.45 ; H, 6.27.

***cis*-1,4-Diphenyl-2-isobutoxy-2-butene-1,4-dione** (**9b**) IR(neat, cm^{-1}) 3066, 3032, 2966, 2936, 2878, 1688, 1659, 1568, 1493, 1470, 1452, 1381, 1313, 1224, 1180, 1075, 1050, 1027, 1004, 967, 949, 872, 849, 824, 781, 756, 712. ^{1}H NMR($CDCl_3$) δ 1.00(6H, d, *J*=6.7 Hz), 2.13(1H, m), 3.90(2H, d, J=6.7 Hz), 6.51(1H, s), 7.39-7.59(6H, m), 7.87-7.97(4H, m). ^{13}C NMR($CDCl_3$) δ 19.01, 27.80, 76.78, 98.09, 128.08, 128.46, 128.71, 128.82, 132.68, 133.53, 134.53, 137.79, 169.16, 188.49, 191.23. *Anal*. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.60; H, 6.71.

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15. The yield of 2-isopropoxy-3-furanone (**6a**) was not fully satisfactory, with PTAB or PHPB(less than 68% yield). It was assumed that steric hindrance of the isopropoxy group predominantly exerted an influence on the decrease in reactivity of 3-alkoxy-2,4,5-triphenylfurans (**3**, **4**). The reaction of ethoxyfurans (**2**) and (**3**) with PTAB in *t*-butyl alcohol did not afforded corresponding 2-*t*-butoxy-3-furanones for 18 h at room temperature.

16. Furil, 4-(2-furoyl)-2-butanone, and 3-(2-furoyl)propanenitrile gave no corresponding furanones with PTAB in ethyl alcohol for 14h at room temperature. 4-(2-Furoyl)-2-butanone and 3-(2-furoyl)-propanenitrile were recovered unchanged with PTAB in DMSO. Furfuryl benzoate did not give

corresponding enediones in moderate yield with PTAB-DMSO. It was assumed that both 3-alkoxy substituent and 2,5-diphenyl moiety were required for the selective transformations of furans to 2-alkoxy-3(2*H*)-furanones and alkoxyenediones.