produced in good yield, and free of the corresponding imine, simply by treating the appropriate lactim ether with an excess of the organolithium reagent. This method therefore constitutes the superior route to these heretofore rare amines.

Experimental Section

The ^1H NMR spectra were recorded on a Varian Associates Model EM-360-A spectrometer at 60 MHz or a Bruker Model WH-90 spectrometer at 90 MHz. The chemical shifts are reported in ppm, downfield from tetramethylsilane. Mass spectral analyses were obtained on an AEI-MS-902 mass spectrometer. The VPC/MS analyses were obtained on a Hewlett-Packard 5985 VPC/MS system. The reaction mixtures were analyzed via VPC on a 20 ft × $^1/_8$ in., 20% SE-30/Anakron-A column utilizing a Varian Associates Model 3920B gas chromatograph. The elemental analyses were performed by MicAnal of Tucson, AZ.

All glassware was oven-dried and flushed with argon prior to use. The diethyl ether and THF were distilled from $LiAlH_4$ prior to use. All lactim ethers were distilled from anhydrous K_2CO_3 and stored under desiccation. All organolithium reagents were standardized in THF, prior to use, with diphenylacetic acid.[17] The 5-methoxy-3,4-dihydro-2*H*-pyrrole, (**1**), 2-methoxy-3,4,5,6-tetrahydropyridine (**2**), and, 7-methoxy-3,4,5,6-tetrahydro-2*H*-azepine (**3**), were prepared via reaction of the corresponding lactam and dimethyl sulfate.[3] The *n*-propyllithium was prepared in ether (0.79 M) from lithium wire and 1-bromopropane by utilizing the method of Evans.[18] The *n*-butyllithium (1.2 M in hexane), methyllithium (1.33 M in ether), *tert*-butyllithium (1.36 M in pentane), and phenyllithium (1.74 M in cyclohexane/ether) were obtained from Alfa. Anhydrous ether was obtained from Mallinckrodt. Diphenylacetic acid, THF, dimethyl sulfate, $LiAlH_4$, 2-pyrrolidinone, 3,4,5,6-tetrahydro-1*H*-pyridin-2-one, and hexahydroazepin-2-one were obtained from Aldrich.

General Procedure for Preparation of Imines 4–6 or 2,2-Dialkyl Amines 7–9 from Lactim Ethers 1–3. An ether solution of the appropriate lactim ether **1–3** in 25 mL of anhydrous ether, cooled to −24 °C (at 25 °C for phenyllithium), was treated with either 1 or 5 equiv of the organolithium reagent, dropwise, over a period of 10 min. The solution was stirred at −24 °C (at 25 °C for phenyllithium) for 12 h, water was added to quench the reaction, the solution was dried (Na_2SO_4), and the solvents were evaporated at reduced pressure to give the products. Samples for NMR and elemental analyses were obtained via preparative VPC. The crude oil was analyzed by VPC for product distribution by using pyridine as an internal standard.[19]

5-*n*-Butyl-3,4-dihydro-2*H*-pyrrole (4c) and 2,2-Di-*n*-butylpyrrolidine (7c). Reaction of 1.826 g (18.40 mmol) of **1** with 15.3 mL of *n*-butyllithium gave an oil containing 0.783 g (6.26 mmol, 34%) of **4c**[3] [^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.21–1.54 (m, 6 H), 1.68–1.93 (m, 2 H), 2.20 (t, 2 H), 3.61 (t, 2 H); mass spectrum, *m/z* (relative intensity) 125 (2, $M^{+\cdot}$), 110 (100), 82 (22), 57 (24), 41 (15)] 0.809 g (4.42 mmol, 24%) of **7c** [^1H NMR ($CDCl_3$) δ 0.91 (t, 6 H), 1.26–1.34 (m, 12 H), 1.56 (t, 2 H), 1.63–1.73 (m, 2 H), 1.81 (s, 1 H), 2.91 (t, 2 H); mass spectrum, *m/z* (relative intensity) 183 (0.1, $M^{+\cdot}$), 127 (14), 126 (100), 96 (6), 82 (4); calcd for $C_{12}H_{25}N$ 183.1983, found 183.2057].

In addition, 0.694 g (6.99 mmol, 38%) of **1** was recovered.

2-Phenyl-3,4,5,6-tetrahydropyridine (5e). Reaction of 0.417 g (3.69 mmol) of **2** and 2.12 mL of phenyllithium gave an oil containing 0.275 g (1.73 mmol, 47%) of **5e**:[20] ^1H NMR ($CDCl_3$) δ 1.60–1.97 (m, 4 H), 2.62 (t, 2 H), 3.63 (t, 2 H), 6.91–7.24 (m, 3 H), 7.44–7.71 (m, 2 H); mass spectrum, *m/z* (relative intensity) 159 (77, $M^{+\cdot}$), 158 (94), 104 (51), 103 (100).

In addition, 0.222 g (1.96 mmol, 53%) of **2** was recovered.

2,2-Di-*n*-butylpyrrolidine (7c). Reaction of 0.327 g (3.30 mmol) of **1** and 7.60 mL of *n*-butyllithium gave an oil containing 0.454 g (2.48 mmol, 75%) of **7c**.[4a]

2,2-Diphenylpiperidine (8e). Reaction of 0.399 g (3.52 mmol) of **2** and 10.1 mL of phenyllithium gave an oil containing 0.500 g (2.11 mmol, 60%) of **8e**: ^1H NMR ($CDCl_3$) δ 1.39–1.81 (m, 4 H), 1.91 (s, 1 H), 2.45 (t, 2 H), 2.80 (t, 2 H), 7.15–7.89 (m, 10 H); mass spectrum, *m/z* (relative intensity) 237 (49, $M^{+\cdot}$), 236 (48), 208 (94), 194 (53), 160 (100); calcd for $C_{17}H_{19}N$ 237.1519; found 237.1517.

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Registry No. **1**, 5264-35-7; **2**, 5693-62-9; **3**, 2525-16-8; **4a**, 872-32-2; **4b**, 872-81-1; **4c**, 64319-86-4; **4d**, 51269-70-6; **4e**, 700-91-4; **5a**, 1462-92-6; **5b**, 1604-01-9; **5c**, 1462-94-8; **5d**, 90949-17-0; **5e**, 57050-07-4; **6a**, 3338-03-2; **6b**, 3338-05-4; **6c**, 3338-06-5; **6d**, 92144-55-3; **6e**, 3338-00-9; **7b**, 92144-56-4; **7c**, 74856-36-3; **7d**, 92144-57-5; **7e**, 68007-29-4; **8b**, 91249-14-8; **8c**, 92144-58-6; **8d**, 92144-59-7; **8e**, 92144-60-0; **9b**, 3311-49-7; **9c**, 3311-50-0; **9d**, 92144-61-1; **9e**, 92144-62-2; **11**, 92144-63-3; MeLi, 917-54-4; PrLi, 2417-93-8; BuLi, 109-72-8; *t*-BuLi, 594-19-4; PhLi, 591-51-5.

Supplementary Material Available: Complete characterization data for all compounds (8 pages). Ordering information is given on any current masthead page.

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(19) The response ratios, relative to pyridine, were determined by utilizing a flame ionization detector on a 20 ft × $^1/_8$ in. 20% SE-30/Anakron-A column: pyridine:**1**:**4**:**7** = 1:1.30:0.88:0.80; pyridine:**2**:**5**:**8** = 1:1.23:0.85:0.80; pyridine:**3**:**6**:**9** = 1:1.33:0.80:0.75.
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Synthesis of Benzofurans from Oxygenated Phenoxyamines

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O-Aryloximes having various oxygenated substitution patterns have been converted to benzofurans, with implications toward natural product synthesis, through an extension of the Fischer indole type of synthesis. The effect of the substituent pattern in the benzene ring and the nature of the carbonyl derived portion of the oxime on benzofuranization were explored.

It is well established that *O*-aryloximes can be converted to benzofurans, presumably through a mechanism paralleling the one postulated for the Fischer indole synthesis.[1] This extension could prove useful in the synthesis of

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Table I. Characterization of Oximes 4

oxime[a]	mp, °C[b]	^{1}H NMR (J in Hz)[d]
4a	113–115	1.67 (m, 6 H), 2.35 (m, 2 H), 2.43 (s, 3 H), 2.62 (m, 2 H), 6.87 (d, 2 H, J = 9), 7.04 (d, 2 H, J = 9), 7.28 (d, 2 H, J = 8), 7.67 (d, 2 H, J = 8)
4b	56.5–57.0	1.6–1.8 (m, 6 H), 2.31 (t, 2 H, J = 6), 2.44 (s, 3 H), 2.61 (t, 2 H, J = 6), 6.52 (ddd, 1 H, J = 1, 2, 8), 6.93 (t, 1 H, J = 2), 7.02 (ddd, 1 H, J = 1, 2, 8), 7.14 (t, 1 H, J = 8), 7.30 (d, 2 H, J = 8), 7.73 (d, 2 H, J = 8)
4c	89–90	1.5–1.7 (m, 6 H), 2.26 (t, 2 H, J = 6), 2.43 (s, 3 H), 2.49 (t, 2 H, J = 6), 6.89 (ddd, 1 H, J = 2, 8, 8), 7.07 (dd, 1 H, J = 2, 8), 7.19 (ddd, 1 H, J = 2, 8, 8), 7.27 (d, 2 H, J = 8), 7.42 (dd, 1 H, J = 2, 8), 7.71 (d, 2 H, J = 8)
4d	103–104[c]	1.74–1.64 (m, 4 H), 2.31–2.26 (m, 2 H), 2.46 (s, 6 H), 2.59–2.54 (m, 2 H), 6.17 (t, 1 H, J = 2), 6.81 (d, 2 H, J = 2), 7.32 (d, 4 H, J = 8), 7.67 (d, 4 H, J = 8)
4e	91–92	2.00 (s, 3 H), 2.03 (s, 3 H), 2.43 (s, 3 H), 6.87 (d, 2 H, J = 9), 7.04 (d, 2 H, J = 9), 7.28 (d, 2 H, J = 8), 7.67 (d, 2 H, J = 8)
4f	66–68	1.99 (s, 3 H), 2.02 (s, 3 H), 2.43 (s, 3 H), 6.53 (ddd, 1 H, J = 1, 2, 8), 6.93 (t, 1 H, J = 2), 7.03 (ddd, 1 H, J = 1, 2, 8), 7.14 (t, 1 H, J = 8), 7.30 (d, 2 H, J = 8), 7.73 (d, 2 H, J = 8)
4g	78–79	1.94 (s, 6 H), 2.43 (s, 3 H), 6.89 (ddd, 1 H, J = 2, 2, 8), 7.02 (dd, 1 H, J = 2, 8), 7.19 (ddd, 1 H, J = 2, 2, 8), 7.29 (d, 2 H, J = 8), 7.40 (dd, 1 H, J = 2, 8), 7.73 (d, 2 H, J = 8)
4h	98.5–99.0	1.94 (s, 3 H), 1.96 (s, 3 H), 2.42 (s, 6 H), 6.16 (t, 1 H, J = 2), 6.78 (d, 2 H, J = 2), 7.29 (d, 4 H, J = 8), 7.64 (d, 2 H, J = 8)

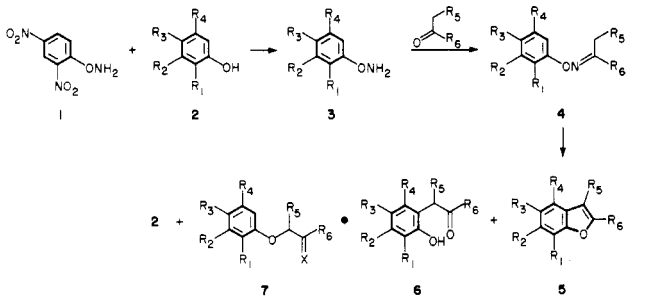
[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all new compounds listed in the table. [b] After crystallization from ethanol. [c] Purified by chromatography on alumina, activity II, eluting with $CHCl_3$. [d] Spectra taken in $CDCl_3$.

variously substituted benzofurans if the *O*-aryloxime precursors, the phenoxyamines **3**, could be obtained.

In a previous report[2] we used an amine exchange reaction (Scheme I), with 2,4-dinitrophenoxyamine (1) as the amine donor and readily obtainable phenols as the amine acceptors, to synthesize in high isolated yields 4-, 3-, and 2-(tosyloxy)phenoxyamine (**3a**, **3b**, and **3c**) and 3,5-bis(tosyloxy)phenoxyamine (**3d**) which have the hydroquinone, resorcinol, catechol, and phloroglucinol substitution patterns, respectively. These compounds ultimately could give benzofurans having tosyloxy substituents which then could be converted to the corresponding hydroxy or methoxy substituents commonly present in natural products. Although a direct route involving amination of phenols already containing the hydroxy or methoxy substituents would have been preferable, such amine acceptors were found to give very poor yields in amine exchange.

In this report we demonstrate the utility of these phenoxyamines **3** for the synthesis of benzofurans **5** in good to excellent yields via the corresponding oximes **4**.

Scheme I. *O*-Aryloxime Rearrangement[a]



[a] **2** and **3**: a, R_3 = OTs; b, R_2 = OTs; c, R_1 = OTs; d, R R_2 = R_4 = OTs. **4**: a, R_3 = OTs; R_5,R_6 = $(CH_2)_4$; b, R_2 = OTs; R_5,R_6 = $(CH_2)_4$; c, R_1 = OTs; R_5,R_6 = $(CH_2)_4$; d, R_2 = R_4 = OTs; R_5,R_6 = $(CH_2)_4$; e, R_3 = OTs; R_6 = CH_3; f, R_2 = OTs; R_6 = CH_3; g, R_1 = OTs; R_6 = CH_3; h, R_2 = R_4 = OTs; R_6 = CH_3. **5**: a, R_3 = OTs; R_5,R_6 = $(CH_2)_4$; b, R_2 = OTs; R_5,R_6 = $(CH_2)_4$; c, R_4 = OTs; R_5,R_6 = $(CH_2)_4$; d, R_1 = OTs; R_5,R_6 = $(CH_2)_4$; e, R_2 = R_4 = OTs; R_5,R_6 = $(CH_2)_4$; f, R_3 = OTs; R_6 = CH_3; g, R_2 = OTs; R_6 = CH_3; h, R_4 = OTs; R_6 = CH_3; i, R_1 = OTs; R_6 = CH_3, j, R_2 = R_4 = OTs; R_6 = CH_3; k, R_1 = OH; R_5,R_6 = $(CH_2)_4$; l, R_1 = OCH_3; R_5,R_6 = $(CH_2)_4$. **6**: a, R_3 = OTs; R_5,R_6 = $(CH_2)_4$; b, R_2 = OTs; R_5,R_6 = $(CH_2)_4$; c, R_4 = OTs; R_5,R_6 = $(CH_2)_4$; d, R_1 = OTs; R_5,R_6 = $(CH_2)_4$; e, R_3 = OTs; R_6 = CH_3. **7**: a, R_3 = OTs; R_5,R_6 = $(CH_2)_4$; X = NH; b, R_2 = OTs; R_5,R_6 = $(CH_2)_4$; X = O.

Results and Discussion

For the benzofuranization of *O*-aryloximes we investigated the cyclohexanone and acetone oximes of **3a–d** as representative cyclic and acyclic examples with respect to the carbonyl derived portion of the molecule. The oximes **4** were synthesized by condensing acetone or cyclohexanone with the appropriate phenoxyamine and in almost all cases could be induced to crystallize from the reaction mixture analytically pure and in good yields (60–80%). Recrystallized or crude phenoxyamine fared equally well in oxime formation.

As the acid catalyst for benzofuranization a formic acid, phosphoric acid mixture was found to be most successful,[3] although an extensive study of such catlysts was not conducted for the oximes reported here.

The Cyclohexanone Oximes. When cyclohexanone *O*-[4-(tosyloxy)phenyl]oxime (**4a**) was treated in a mixture of formic and phosphoric acids (10/1) at 60 ° C only a 16% yield of 8-tosyloxy-1,2,3,4-tetrahydrodibenzofuran (**5a**) was obtained (Scheme I). Isolation of lower R_f products by liquid chromatography showed that 4-(tosyloxy)phenol (**2a**) plus one other phenol had been produced in 12% and 72% yields, respectively. Identification of the new phenol was complicated by spectral data which indicated a mixture of two compounds and which was contradicted by chromatographic data, indicating a single compound. Working on the suspicion that the new phenol was the phenolic ketone **6a**, the hydrated form of **5a**, we treated this compound with dimethyl sulfate. The resulting product now gave both spectral and chromatographic data consistent for a single compound identified as 4-(tosyloxy)-2-(2-oxocyclohexyl)anisole (**6a** methyl ether). The initial confusion caused by the spectral data for **6a** was probably due to an equilibrium existing between **6a** and its hemiketal form.

The formation of **6a** no doubt comes from hydrolysis during isolation of the intermediate imine **9** which results from the 3,4-oxaza-Cope rearrangement postulated for benzofuranization (Scheme II). Such imine intermediates as well as their hydrolysis products also have been found by others.[1]

Although the initial yield of benzofuran **5a** from oxime **4a** was quite low, the major product of the reaction, **6a**, is simply the hydrated form of **5a**. A sample of phenolic ketone **6a** could be dehydrated quantitatively to **5a** by

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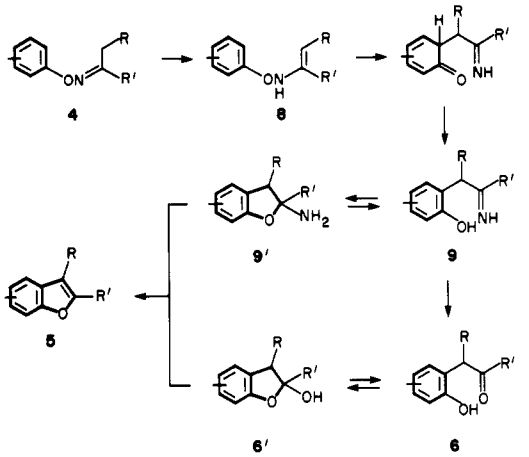
Scheme II. Mechanism of Benzofuranization of *O*-Aryloximes



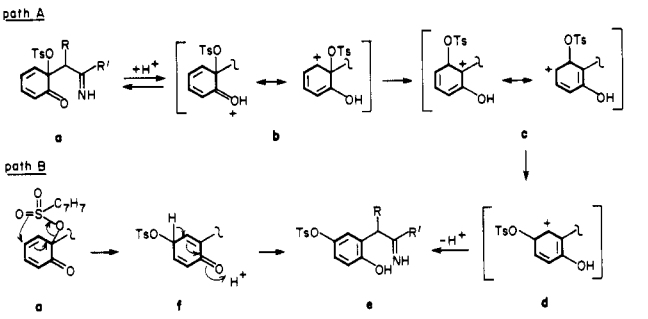
stirring in methanesulfonic acid at room temperature. By applying this dehydration procedure to the crude product mixture an overall 82% yield of **5a** was realized. Thus a two stage acid treatment of **4a** (HCO_2H/H_3PO_4 at 60 °C followed by dehydration of the crude reaction mixture with $MeSO_3H$) gives a high yield of benzofuran.

With cyclohexanone *O*-[3-(tosyloxy)phenyl]oxime (**4b**) the oxime is no longer symmetrical as was the case with **4a** so there is the added complication that the 3,4-oxaza-Cope rearrangement can occur at either of two sites. Rearrangement to the position para to the tosyloxy substituent gave **5b** (36%) while rearrangement to the ortho position gave **5c** (6%), both obtained after heating **4b** in HCO_2H/H_3PO_4 at 60 °C. Also isolated were 3-(tosyloxy)phenol (**2b**), 5-(tosyloxy)-2-(2-oxocyclohexyl)phenol (**6b**), 3-(tosyloxy)-2-(2-oxocyclohexyl)phenol (**6c**), and 2-[3-(tosyloxy)phenoxy]cyclohexanone (**7b**) in 13%, 18%, 2%, and 10% yields, respectively.

As with **6a**, identification of **6b** and **6c** required methylation to the anisoles. Their formation again results from trapping of the imine intermediate in the benzofuranization pathway. For the α-phenoxy ketone **7b** the structural assignment was proved by spectral and chromatographic identity with the product obtained by condensing 3-(tosyloxy)phenol and α-chlorocyclohexanone. A precedent for formation of such a compound is found in the benzofuranization of acetone *O*-(4,8-dimethylcoumar-7-yl)oxime which gave a 5% yield of 7-(acetonyloxy)-4,8-dimethylcoumarin as a side product in the synthesis of 4,5',8-trimethylpsoralen.[3] When as an analogy the work reported with *S*-arylthiooximes[4] was used, a possible mechanism for the production of **7b** can be deduced. In this mechanism the ene–phenoxyamine intermediate (**8**), instead of undergoing a 3,4-oxaza-Cope rearrangement, rearranges via a four-centered transition state to give imine **7a**. Hydrolysis under the isolation conditions then gives **7b**. Alternatively, **4b** may undergo hydrolysis to give **3b** and cyclohexanone. The enol form of the latter may then attack protonated **3b** to give **7b**.

Because **4b** gives signficant quantities of **6b** and **6c** under mild conditions, we were able to extend the reaction so that the imine precursors were completely converted to **5b** and **5c**. This was accomplished when the reaction of **4b** in HCO_2H/H_3PO_4 at 60 °C was continued at reflux. We then obtained **5b** and **5c** in 55% and 23% yields, respectively. This two stage heat treatment (HCO_2H/H_3PO_4 at 60 °C followed by refluxing) should serve as a complement to the two-step acid treatment described for **4a**. It should be noted that the preponderance of **5b** formed in this reaction was to be expected based solely on steric considerations.

Scheme III. Mechanism of Tosyloxy Migration during Benzofuranization



Cyclohexanone *O*-[2-(tosyloxy)phenyl]oxime (**4c**) has a potential rearrangement site already occupied by a tosyloxy substituent as well as an unoccupied site. Based on Fischer indole chemistry[5] one expected that a 3,4-oxaza-Cope rearrangement to the occupied ortho position would afford 9-(tosyloxy)-1,2,3,4-tetrahydrodibenzofuran (**5c**) where the substituent has undergone a 1,2-migration. However, when **4c** was heated in HCO_2H/H_3PO_4 at 60 °C and the reaction interrupted upon consumption of educt, a 3% yield of **5a** was obtained along with a 13% yield of 6-(tosyloxy)-1,2,3,4-tetrahydrodibenzofuran (**5d**). The latter compound was expected from rearrangement to the unoccupied position. The identity of the unexpected benzofuran was confirmed by its spectral and chromatographic equivalence to the benzofuran obtained from oxime **4a** and by its nonequivalence with **5c** which had been prepared from oxime **4b**. In addition we have confirmed (by HPLC) that **4c** was uncontaminated by its **4a** isomer, thus ruling this out as a source of the isolated **5a**.

There are two mechanisms that can be proposed for the production of **5a** from **4c** as presented in Scheme III. The significant difference between these mechanisms is that one requires a stepwise migration of the tosyloxy substitution involving two 1,2-shifts while the other requires a concerted migration. Of these possiblities the latter is favored because no benzofuran **5c** could be found by HPLC. If a stepwise migration of the tosyloxy substituent were taking place, then one would expect some of imine **9** formed after the first 1,2 migratory shift to go on to **5c**.

From the more polar fraction we obtained 2-(tosyloxy)phenol (**2c**), 6-(tosyloxy)-2-(2-oxocyclohexyl)phenol (**6d**), and **6a** in 37%, 19%, and 2% yields, respectively. In contrast to the other phenolic ketones, methylation of **6d** to the anisole was not required in order to obtain definitive spectral data. The phenolic ketone again represents a signficiant amount of reaction product which could be transformed to benzofuran. With the two stage heat treatment (HCO_2H/H_3PO_4 at 60 °C followed by reflux) **5d** and **5a** were obtained in 40% and 4% yield, respectively. As a comparison, the two stage acid treatment (HCO_2H/H_3PO_4 followed by $MeSO_3H$) gave a 45% and 5% yield of **5d** and **5c**, showing that the two reaction protocols give the same results. Either starting off immediately at reflux or substituting $MeSO_3H$ for H_3PO_4 gave greater amounts of 2-(tosyloxy)phenol (**2c**).

For all the oximes studied heating in HCO_2H/H_3PO_4 results in the formation of phenol formally arising from

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(5) Ishii, H. *Acc. Chem. Res.* **1981**, *14*, 275.

Table II. Properties of Benzofurans 5

benzofuran[a]	mp, °C	^{1}H NMR (J in Hz)[e]	UV λ_{max} nm (ϵ)[f]
5a	130–131[b]	1.8–2.0 (m, 4 H), 2.43 (s, 3 H), 2.4–2.5 (m, 2 H), 2.6–2.8 (m, 2 H), 6.67 (dd, 1 H, J = 2, 9), 7.11 (d, 1 H, J = 2), 7.20 (d, 1 H, J = 9), 7.28 (d, 2 H, J = 8), 7.70 (d, 2 H, J = 8)	256 (10 430), 281s (3 860),[g] 288s (3 290),
5b	117–119[c]	1.8–2.0 (m, 4 H), 2.43 (s, 3 H), 2.56 (t, 2 H, J = 6), 2.70 (t, 2 H, J = 6), 6.81 (dd, 1 H, J = 2, 8), 7.03 (d, 1 H, J = 2), 7.23 (d, 1 H, J = 8), 7.28 (d, 2 H, J = 8), 7.69 (d, 1 H, J = 8)	257 (12 000), 272s (6 140), 280s (4 860), 289s (3 570),
5c	113.5–115.5[c]	1.8–2.0 (m, 4 H), 2.46 (s, 3 H), 2.7–2.8 (m, 4 H), 6.55 (d, 1 H, J = 8), 6.99 (t, 1 H, J = 8), 7.28 (d, 1 H, J = 8), 7.33 (d, 2 H, J = 8), 7.76 (d, 2 H, J = 8)	256 (12 710), 284s (2 860),
5d	111–113[d]	1.7–1.9 (m, 4 H), 2.43 (s, 3 H), 2.5–2.6 (m, 4 H), 6.90 (dd, 1 H, J = 1, 8), 7.06 (t, 1 H, J = 8), 7.26 (dd, 1 H, J = 1, 8), 7.27 (d, 2 H, J = 8), 7.76 (d, 2 H, J = 8)	255 (13 570), 284s (2 140),
5e	124–125[b]	1.8–1.9 (m, 4 H), 2.45 (s, 3 H), 2.48 (s, 3 H), 2.7–2.6 (m, 4 H), 6.38 (d, 1 H, J = 2), 6.88 (d, 1 H, J = 2), 7.31 (d, 2 H, J = 8), 7.35 (d, 2 H, J = 8), 7.65 (d, 2 H, J = 8), 7.71 (d, 2 H, J = 8)	262 (19 870), 280s (8 670), 290s (5 680),
5f	88–89[b]	2.42 (d, 3 H, J = 1), 2.43 (s, 3 H), 6.30 (q, 1 H, J = 1), 6.73 (dd, 1 H, J = 2, 9), 7.12 (d, 1 H, J = 2), 7.23 (d, 1 H, J = 9), 7.28 (d, 2 H, J = 8), 7.68 (d, 2 H, J = 8)	247 (14 050), 273 (4 010), 279 (4 090), 286 (3 860),
5g	81.5–82.0[d]	2.43 (d, 3 H, J = 1), 2.45 (s, 3 H), 6.33 (q, 1 H, J = 1), 6.80 (dd, 1 H, J = 2, 8), 7.06 (d, 1 H, J = 2), 7.30 (d, 2 H, J = 8), 7.30 (d, 1 H, J = 8), 7.71 (d, 2 H, J = 8)	249 (12 160), 274 (4 010), 286 (3 150),
5h	111–112[d]	2.41 (d, 3 H, J = 1), 2.45 (s, 3 H), 6.28 (q, 1 H, J = 1), 6.69 (dd, 1 H, J = 1, 8), 7.04 (t, 1 H, J = 8), 7.30 (d, 3 H, J = 8), 7.30 (d, 1 H, J = 8), 7.72 (d, 2 H, J = 8)	248 (13 300), 272 (3 450), 281 (2 390),
5i	92–94[d]	2.27 (d, 3 H, J = 1), 2.43 (s, 3 H), 6.29 (q, 1 H, J = 1), 6.95 (dd, 1 H, J = 1, 8), 7.07 (t, 1 H, J = 8), 7.27 (d, 2 H, J = 8), 7.32 (dd, 1 H, J = 1, 8), 7.75 (d, 2 H, J = 8)	248 (11 740), 274 (2 580), 283 (1 740),
5j	oil[b]	2.38 (d, 3 H, J = 1), 2.46 (s, 6 H), 6.26 (q, 1 H, J = 1), 6.44 (d, 1 H, J = 2), 6.96 (d, 1 H, J = 2), 7.31 (d, 4 H, J = 8), 7.65 (d, 2 H, J = 8), 7.67 (d, 2 H, J = 8)	254 (13 810), 272 (5 670), 285s (3 270)

[a] Satisfactory analytical data (±0.3% for C, H) were reported for all new compounds listed in the table. [b] Purified by chromatography on SiO_2, eluting with CH_2Cl_2/hexane, 60/40. [c] Purified by MPLC (column B, CH_2Cl_2/hexane, 60/40). [d] Purified by HPLC (column A, hexane/CH_2Cl_2, 65/35). [e] Spectra taken in $CDCl_3$. [f] Spectra taken in CH_3OH. [g] A shoulder is designated by s.

N–O bond cleavage in the oxime. With **4c** this side reaction was especially severe, since a 37% yield of **2c** was obtained. Why this is the case is still obscure for the fate of the cyclohexyl part of the oxime is still unknown. Possibilities for the side reaction include a Beckman rearrangement[6] or heterolytic N–O bond cleavage leading to phenoxenium ions.[7] We are currently investigating such possibilities.

To complete the investigation of the cyclohexanone oximes, cyclohexanone *O*-[3,5-bis(tosyloxy)phenyl]oxime (**4d**) was subjected to the two stage heat treatment. From this we obtained an 87% yield of 7,9-bis(tosyloxy)-1,2,3,4-tetrahydrodibenzofuran (**5e**) and an 8% yield of 3,5-bis(tosyloxy)phenol (**2d**).

Acetone Oximes. With the cyclohexanone oximes the 3,4-oxaza-Cope rearrangement takes place onto a disubstituted carbon in the ketone-derived portion of the oxime. To see if rearrangement would occur to a methyl carbon as well, the corresponding acetone oximes **4e–h** were subjected to the two stage acid treatment.

With acetone *O*-[3,5-bis(tosyloxy)phenyl]oxime (**4h**), we obtained an 85% yield of 2-methyl-4,6-bis(tosyloxy)-benzofuran (**5j**) and a 9% yield of **2d**. These results are identical with those experienced with the corresonding cyclohexanone oxime, **4d**. As can be seen in Table IV, the other acetone oximes gave poorer yields than their cyclohexanone oxime counterparts. A notable exception is acetone *O*-[2-(tosyloxy)phenyl]oxime (**4g**) which gave a mixture of benzofurans in 55% yield. This yield was similar to those obtained for the other acetone oximes **4e** and **4f** (60%). With cyclohexanone *O*-[2-(tosyloxy)-phenyl]oxime (**4c**), however, a significantly lower yield (49%) was obtained compared to the other cyclohexanone oximes **4a** and **4b** (>80%).

To determine why the acetone oximes were giving lower yields acetone *O*-[4-(toxyloxy)phenyl]oxime (**4e**) was heated in HCO_2H/H_3PO_4 at 60 °C. The reaction was interrupted upon complete consumption of **4e**, thinking that side products which might not survive a subsequent reflux could now be isolated. From **4e** we obtained a 47% yield of benzofuran **5f** and in the lower R_f products we found 4-(tosyloxy)-2-(2-oxopropyl)phenol (**6e**) and **2a** in 12% and 7% yields, respectively. Also isolated were two fractions A and B which accounted for 10% and 11% of the initial reaction mass. Although each of these fractions gave a single spot on TLC, HPLC analysis showed them to be composed of a multitude of products as yet unidentified.

Other comparisons of note between the acetone and cyclohexanone oximes lie in the composition of the benzofuran mixtures obtained with **4b**, **4c**, **4f**, and **4g**. For the acetone oxime **4f**, a 1.4/1 mixture of 2-methyl-6-(tosyloxy)benzofuran (**5g**) to 2-methyl-4-(tosyloxy)benzofuran (**5h**) was obtained which shows that the 3,4-oxaza-Cope rearrangement occurs preferentially to the less sterically hindered position. However, this preference has decreased from the 2.4/1 ratio found for the cyclohexanone oxime **4b**. This decrease probably reflects the decreased steric demands imposed by the less substituted α-carbon in the carbonyl portion of the acetone oxime.

With acetone oxime **4g** we obtained a 5/1 mixture of 2-methyl-7-(tosyloxy)benzofuran (**5i**) to 2-methyl-5-(to-

(6) Treatment of oxime acetates with aluminum chloride resulted in a Beckmann rearrangement and not the desired α-acetoxy imines [House, H. O.; Richey, F. A., Jr. *J. Org. Chem.* **1969**, *34*, 1430.]

(7) Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1982**, *104*, 6393.

Table III. Characterization of Phenols 6a, 6d, and 6e, Methyl Ethers of 6a, 6b, and 6c, and Ketone 7b

compd[a]	mp, °C	^{1}H NMR (J in Hz)[c]	UV λ_{max} nm (ϵ)[e]
6a	130–130.5 ($CHCl_3$/hexane)	*d*	276 (3270)
6a methyl ether	oil[b]	1.5–2.2 (m, 6 H), 2.43 (s, 3 H), 2.45 (dd, 2 H, J = 5, 10), 3.73 (s, 3 H), 3.86 (dd, 1 H, J = 1, 9), 6.63 (d, 1 H, J = 3), 6.72 (d, 1 H, J = 9), 6.83 (dd, 1 H, J = 3, 9), 7.30 (d, 2 H, J = 8), 7.68 (d, 2 H, J = 9)	
6b methyl ether	86–87[b]	1.6–2.3 (m, 6 H), 2.44 (s, 3 H), 2.4–2.5 (m, 2 H), 3.65 (s, 3 H), 3.87 (dd, 1 H, J = 6, 13), 6.49 ((dd, 1 H, J = 2, 8), 6.54 (d, 1 H, J = 8), 6.97 (d, 1 H, J = 8), 7.32 (d, 2 H, J = 8), 7.75 (d, 2 H, J = 8)	278s (3070), 273 (3820)
6c methyl ether	oil[b]	1.5–2.4 (m, 6 H), 2.45 (s, 3 H), 3.71 (dd, 1 H, J = 6, 12), 3.74 (s, 3 H), 6.63 (dd, 1 H, J = 1, 8), 6.79 (dd, 1 H, J = 1, 8), 7.13 (t, 1 H, J = 8), 7.33 (d, 2 H, J = 8), 7.77 (d, 2 H, J = 8)	273 (3030), 269 (2960)
6d	133–135 ($CHCl_3$/hexane)	1.8–2.4 (m, 6 H), 2.45 (s + m, 5 H), 3.94 (dd, 1 H, J = 5, 12), 6.23 (bs, 1 H), 6.69 (dd, 1 H, J = 2, 7), 6.75 (t, 1 H, J = 7), 6.99 (dd, 1 H, J = 2, 7), 7.33 (d, 2 H, J = 8), 7.75 (d, 2 H, J = 8)	274 (3270)
6e	82–83.5 ($CHCl_3$/hexane)	2.24 (s, 3 H), 2.44 (s, 3 H), 3.65 (s, 2 H), 6.70 (dd, 1 H, J = 3, 9), 6.74 (d, 1 H, J = 9), 6.77 (d, 1 H, J = 3), 7.30 (d, 2 H, J = 8), 7.68 (d, 2 H, J = 8)	273 (2780)
7b	98–99[b]	1.7–2.4 (m, 6 H), 2.44 (s, 3 H), 2.5–2.7 (m, 2 H), 4.55 (ddd, 1 H, J = 1, 5, 11), 6.49 (t, 1 H, J = 2), 6.59 (ddd, 1 H, J = 1, 2, 8), 6.75 (ddd, 1 H, J = 1, 2, 8), 7.12 (t, 1 H, J = 8), 7.30 (d, 2 H, J = 8), 7.69 (d, 2 H, J = 8)	273 (2600), 268 (2480)

[a] Satisfactory analytical data (±0.3% for C, H) were reported for all new compounds listed in the table except **6c** methyl ether which was characterized by high-resolution mass spectrometry (calcd for $C_{20}H_{22}O_5S$, m/z 374.1189, found 374.1195). [b] Purified by chromatography on silica, eluting with hexane/$CHCl_3$/EtOAc, 47/31/22. [c] Spectra taken in $CDCl_3$. [d] Due to the equilibrium between phenolic ketone and hemiketal forms, this proton spectrum was very complex. [e] Spectra taken in CH_3OH.

syloxy)benzofuran (**5f**). As with the corresponding cyclohexanone oxime **5c** the minor benzofuran has arisen from the oxaza-Cope rearrangement to the occupied position followed by concerted migration of the tosyloxy group. The structural assignment for the minor benzofuran was confirmed by its chromatographic and spectral identity with **5f** obtained from oxime **4e**. The preference, however, for rearrangement to the unoccupied position has dropped from the 10/1 ratio found for **4c**. Again, this may reflect the decreased steric demands imposed by the α-carbon of the carbonyl derived part of the oxime.

All of the oxygen-substituted benzofurans which we have described in this report have been restricted to sulfonates as required by the amine exchange reaction in order to form the phenoxyamine precursors. After oxime formation and rearrangement, the sulfonate group is no longer needed and can be removed. To this end, we subjected 6-(tosyloxy)-1,2,3,4-tetrahydrodibenzofuran (**5d**) to hydrolysis by using potassium hydroxide in methanol. Although we did obtain the desired benzofuranol **5k**, a significnt amount of 6-methoxy-1,2,3,4-tetrahydrodibenzofuran (**5l**) was also obtained, resulting from methoxide acting as a competing nucleophile. For reaction conditions that can only have hydroxide as a nucleophile, we treated **5d** with tetraethylammonium hydroxide in refluxing THF to give a quantitative yield of 4-hydroxy-6,7,8,9-tetrahydrodibenzofuran (**5k**).

Conclusion

We have synthesized benzofurans from *O*-aryloximes with oxygenated substitution patterns similar to those found in natural products. The *O*-aryloximes chosen for study show that the following: (1) The 3,4-oxaza-Cope rearrangement involved in benzofuranization will take place to the greater extent to the less hindered position on the aromatic ring with this preference being influenced by branching in the carbonyl derived portion of the oxime. (2) Substitution at a potential rearrangement site in the aromatic ring does not prevent rearrangement to that site and may lead to migraton of that substituent. (3) Under identical reaction conditions oximes whose rearrangement sites in the carbonyl derived portion are methylene carbons give better yields than oximes where these sites are methyl carbons. A summary of these results is presented in Table IV.

Table IV. Yields of Benzofurans (5) and Phenols (2) from Oxime (4)

oxime	benzofuran (% yield)	phenol (% yield)	oxime	benzofuran (% yield)	phenol (% yield)
4a	**5a** (82)	**2a** (12)	**4e**	**5f** (61)	**2a** (7)
4b	**5b** (55)	**2b** (13)	**4f**	**5g** (35)	**2b** (7)
	5c (23)			**5h** (25)	
4c	**5d** (44.5)	**2c** (37)	**4g**	**5i** (46)	**2c** (14)
	5a (4.5)			**5f** (9)	
4d	**5e** (87)	**2d** (8)	**4h**	**5j** (85)	**2d** (9)

Experimental Section

General Methods. All melting points are uncorrected. ^{1}H NMR chemical shifts are expressed in ppm downfield from internal Me_4Si. Elemental analyses were performed by the Analytical Laboratory, College of Chemistry, University of California, Berkeley. High-pressure liquid chromatography (HPLC) was done with a Whatman M-9 50-cm preparative metal column (column C). Preparative medium-pressure liquid chromatography (MPLC) was done by using Ace Michel-Miller glass columns (column A, 22 × 300 mm; column B, 37 × 350 mm) packed with 40–63 μm silica gel 60 (E. Merck). Analytical thin-layer chromatography (TLC) was done with aluminum-backed silica plates (E. Merck). Preparative TLC was carried out on 2000 μm silica gel GF(Analtech). Benzene and dimethylformamide (DMF) were dried over CaH_2. Organic layers were washed with brine, dried over magnesium sulfate, filtered, and evaporated using a rotary evaporator.

General Synthesis of the Oximes 4.[8] In a typical reaction, 4.0 mmol of **3** along with 4.0 mmol of ketone and 2 drops of concentrated HCl in 20 mL of absolute EtOH were heated to reflux whereupon the heat source was immediately removed. The oximes produced were isolated in the following manner: **4a**, **4b**, **4c**, **4e**, **4f**, **4g**, and **4h**. These oximes crystallized after chilling the reaction mixture to 0 °C. Addition of water was sometimes required to induce crystallization. **4d**: The reaction mixture was diluted 5-fold with ether and washed with 0.5 N NaOH. From the organic layer was obtained an oil which was chromatographed on neutral alumina (activity II) eluting with $CHCl_3$. Data on these oximes are collected in Table I.

General Procedures for the Synthesis of Phenolic Ketones 6 from *O*-Aryloximes 4. In a typical reaction 2.0 mmol of the oxime was heated in a mixture of 60 mL of HCO_2H (95–97%)

(8) Sheradsky, T. *J. Heterocycl. Chem.* **1967**, *4*, 413.

and 6.0 mL of H_3PO_4 (85%) to 60 °C. The reaction course was followed by TLC (60/40, CH_2Cl_2/hexane).

For the isolation of **6**, immediately after educt has been consumed, the reaction mixture was poured into 400 mL of cold water and extracted with Et_2O (1 × 320 mL, 3 × 160 mL). The combined organic phase was washed with saturated $NaHCO_3$ (3 × 300 mL), dried, and concentrated to give a residue which was chromatographed on silica. Elution with 60/40, CH_2Cl_2/hexane gave benzofuran **5**. Subsequent elution with 43/34/23, EtOAc/hexane/$CHCl_3$ gave a residue containing **6** which was purified further in the following manner. From Oxime **4a**: Purification was by MPLC (Column A). Elution with 42/29/29, hexanes/EtOAc/$CHCl_3$ at 15 mL/min separates **6a** (t_R 13 min) from **2a** (t_R 9 min). From Oxime **4b**: Purification was by MPLC (Column B). Elution with 47/31/22, hexanes/$CHCl_3$/EtOAc at 20 mL/min separates **7b** (t_R 34 min), **2b** (t_R 38 min), **6b** (t_R 48 min), and **6c** (t_R 59 min). From Oxime **4c**: Purification was by MPLC (Column A). Elution with 50/33/17, hexane/$CHCl_3$/EtOAc at 5 mL/min separates **3c** (t_R 5.3 min) and **6d** (t_R 7.8 min). Compound **6a** was first separated on a gravity column [TLC 50/33/17, hexanes/$CHCl_3$/EtOAc) t_R 0.15]. From Oxime **4e**: From a gravity column a mixture of **2a** and **6e** free from other reaction products was obtained; TLC (47/31/22, hexanes/$CHCl_3$/EtOAc) **2a**, R_f 0.26; **6e**, R_f 0.22. Separation was effected by preparative TLC.

Data on resulting phenolic ketones are collected in Table III.

Synthesis of Methyl Ethers of Phenolic Ketones 6a, 6b, and 6c. In a typical reaction 0.1 mmol of the phenolic ketones was stirred under N_2 at room temperature in 1 mL of MeCN along with 28 mg (0.2 mmol) of finely ground K_2CO_3 to which was added 38 μL of Me_2SO_4 (0.4 mmol). After 2 h the MeCN was evaporated, and 1 mL of 2.8 M aqueous glycine was added to the residue which was then heated to 50 °C for 0.5 h. The reaction mixture was diluted with water (15 mL) and extracted with Et_2O (3 × 10 mL). The combined organic phase was extracted with 0.5 N NaOH (2 × 15 mL), dried, and concentrated to give the anisoles which were purified in the following manner: **6a** methyl ether was obtained directly in high purity; TLC (95/5 benzene/MeOH) R_f 0.52. **6b** methyl ether was purified by column chromatography on silica with 47/31/22, hexanes/$CHCl_3$/EtOAc; TLC (95/5, benzene/MeOH) R_f 0.40. **6c** methyl ether was purified by MPLC (column B), eluting with 47/31/22, hexanes/$CHCl_3$/EtOAc at 20 mL/min, t_R 37 min; TLC (95/5, benzene/MeOH) R_f 0.38.

General Synthesis of Benzofurans 5 from *O*-Aryloximes 4. Method A. Two Stage Acid Treatment. Typically, 0.5 mmol of oxime was heated in a 10/1 mixture of HCO_2H/H_3PO_4 at 60 °C. After consumption of educt, isolation proceeded as described in the synthesis of the phenolic ketones. To the crude reaction product was then added 2 mL of $MeSO_3H$ at 10 °C and after stirring for 1 h under N_2 the reaction mixture was poured into cold water (20 mL) and extracted with Et_2O (2 × 15 mL). The combined organic phase was washed with saturated $NaHCO_3$ (1 × 15 mL) and 0.5 N NaOH (3 × 15 mL), dried, and concentrated to give crude benzofuran which was purified on a gravity silica column with 60/40, CH_2Cl_2/hexane. For benzofuran **5a** obtained from **4a** no further purification was required. From oxime **4c** a mixture of benzofurans (**5a** and **5d**) was obtained. Benzofuran **5d** was separated by using column C, eluting with 65/35, hexanes/CH_2Cl_2 at 6.0 mL/min: t_R **5a** 30.6 min; t_R **5d** 27.9 min.

Method B. Two Stage Heat Sequence. The initial reaction was conducted as in method A. When oxime **4** (0.5 mmol) had been consumed the reaction was heated to reflux for 1 h. After cooling the reaction mixture was poured into cold water (100 mL) and extracted with Et_2O (1 × 80 mL, 3 × 40 mL). The combined organic phase was washed with saturated $NaHCO_3$ (3 × 50 mL) and 0.5 N NaOH (1 × 80 mL, 2 × 40 mL), dried, and concentrated. The residues were purified by gravity silica column eluting with 60/40, C_2Cl_2/hexanes to give benzofurans **5**. For benzofurans **5a** (from oxime **4a**), **5e**, **5f** (from oxime **4e**), and **5j** no further purification was required. From oximes **4b**, **4c**, **4f**, and **4g** mixtures of benzofurans were obtained which were purified in the following manner: From oximes **4b**, **4c**, **4f**, and **4g** mixtures of benzofurans were obtained which were purified in the following manner: From oxime **4b** purification was by MPLC (column B) eluting with 60/40, CH_2Cl_2/hexanes at 15 mL/min; t_R **5b** 57.5 min, t_R **5c** 41.0 min; HPLC (column C) 65/35, hexane/CH_2Cl_2 at 6.0 mL/min; t_R **5b** 30.6 min, t_R **5** c 18.8 min. From oxime **4c** purification was as in the synthesis of **5d** by the two stage heat treatment. From oxime **4f** purification was by HPLC (column C) eluting with 65/35, hexanes/CH_2Cl_2 at 6.0 mL/min; t_R **5g** 28.6 min, t_R **5h** 20.8 min. From oxime **4g** purification was by HPLC (column C) as above; t_R **5i** 28.2 min, t_R **5f** 33.4 min.

For the recovery of **2** the combined 0.5 N NaOH extracts were acidified to pH 6 with 1 N H_2SO_4 and extracted with Et_2O (1 × 80 mL, 2 × 40 mL). The combined organic phase was dried and concentrated to give phenols **2** which were further purified by silica column chromatography using 47/31/22, hexane/$CHCl_3$/EtOAc.

Characterization data for the benzofurans are summarized in Table II.

2-[3-(Tosyloxy)phenoxy]cyclohexanone (7b). To 2.64 g (10 mmol) of 3-(tosyloxy)phenol[9] and 1.66 g (12 mmol) of finely grounded K_2CO_3 in 14 mL of DMF and 14 mL of benzene stirred under N_2 at room temperature was added 1.59 g (12 mmol) α-chlorocyclohexanone.[10] After heating to 80 °C for 20 min an additional 0.32 g of α-chlorocyclohexanone was added with heating continued for another 1.5 h. The solvents were evaporated and the resulting residue was partitioned between $CHCl_3$ (60 mL) and water (60 mL). The aqueous layer was then extracted with $CHCl_3$ (1 × 40 mL) and the combined organic phase was extracted with 0.5 N NaOH (4 × 50 mL), dried, and concentrated to give a residue which was triturated with hexane. After purification by column chromatography (SiO_2) with 47/31/22, hexanes/$CHCl_3$/EtOAc, 406 mg (11% yield) of **7b** was obtained: TLC R_F 0.33.

4-Hydroxy-6,7,8,9-tetrahydrodibenzofuran (5k). A solution of 102 mg (0.3 mmol) of **5d** and 708 mg of a 25% aqueous solution of tetraethylammonium hydroxide (~1.2 mmol ^-OH) in 5 mL of THF was degassed by purging with N_2 and then heated to reflux for 8 h. After cooling the reaction mixture, it was poured into 50 mL of cold 0.5 M H_2SO_4 and extracted with Et_2O (2 × 25 mL). The combined organic phase was dried and concentrated to give 58 mg (100% yield) of **5k**: TLC (60/40 CH_2Cl_2/hexane) R_f 0.19; mp 120–122 °C (hexane) (lit.[11] mp 117–118 °C); ^1H NMR ($CDCl_3$) δ 1.8–2.0 (m, 4 H), 2.6 (m, 2 H), 2.7–2.8 (m, 2 H), 5.32 (bs, 1 H), 6.75 (dd, 1 H, J = 1, 8 Hz), 6.97 (dd, 1 H, J = 1, 8 Hz), 7.06 (t, 1 H, J = 8 Hz); UV (MeOH) λ_{max} 255 nm (ε 13 571), 250 (13 083).

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Registry No. **2a**, 35616-03-6; **2b**, 18622-12-3; **2c**, 35616-01-4; **2d**, 20032-62-6; **3a**, 89232-65-5; **3b**, 89232-59-7; **3c**, 89232-63-3; **3d**, 89232-61-1; **4a**, 92346-02-6; **4b**, 92346-03-7; **4c**, 92346-04-8; **4d**, 92346-05-9; **4e**, 92346-06-0; **4f**, 92346-07-1; **4g**, 92346-08-2; **4h**, 92346-09-3; **5a**, 92346-10-6; **5b**, 92346-11-7; **5c**, 92346-12-8; **5d**, 92346-13-9; **5e**, 92346-14-0; **5f**, 92346-15-1; **5g**, 92346-16-2; **5h**, 92346-17-3; **5i**, 92346-18-4; **5j**, 92346-19-5; **5k**, 91962-69-5; **6a**, 92346-20-8; **6a** (methyl ether), 92346-21-9; **6b**, 92346-22-0; **6b** (methyl ether), 92365-84-9; **6c**, 92346-23-1; **6c** (methyl ether), 92346-24-2; **6d**, 92346-25-3; **6e**, 92346-26-4; **7b**, 92346-27-5; Me_2SO_4, 77-78-1; α-chlorocyclohexanone, 822-87-7; cyclohexanone, 108-94-1; acetone, 67-64-1.

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