Tetrahedron Vol. 48, No. 38, pp. 8179-8188, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Synthesis of 6*H*-Dibenzo[*b*,*d*]pyran-6-ones via Dienone-Phenol Rearrangements of Spiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'-ones

David J. Hart*, Adrienne Kim, Ramanarayanan Krishnamurthy, Gregory H. Merriman, Anne-Marie Waltos

Department of Chemistry, The Ohio State University
120 W. 18th Ave., Columbus, Ohio 43210

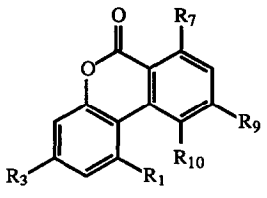
(*Received in USA* 5 *May* 1992)

Key Words: dienone-phenol rearrangement; 6H-dibenzo[*b*,*d*]pyran-6-one, spiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'-one

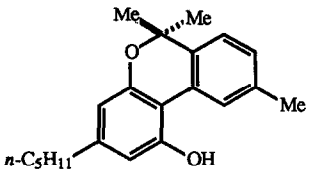
Abstract. A series of spiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'-ones were prepared from metallated benzamides and 4,4-dimethoxycyclohexadienone. Rearrangement of these spirodienones under a variety of conditions gave substituted 6*H*-dibenzo[*b*,*d*]pyran-6-ones. Rearrangements in aqueous sulfuric acid gave products of formal O-migration while rearrangements in trifluoroacetic anhydride-trifluoroacetic acid-sulfuric acid usually gave C-migration products.

Substituted 6*H*-dibenzo[*b*,*d*]pyran-6-ones are widespread in nature. For example, fasciculiferol (**1**) and alternariol (**2**) have been isolated from the heartwood of trees,[1] autumnarial (**3**) has been obtained from lilies,[2] and dibenzopyranones **4** and **5** have been isolated from plants that grow in the Western Himalayas as well as scent gland secretions from beaver.[3,4] In addition, 6*H*-dibenzo[*b*,*d*]pyran-6-ones have been used as late intermediates in the synthesis of cannibinol (**6**) and other cannabinoids,[5] appear as a substructure in the defucogilvocarcin (**7**) and related natural products,[6] and exhibit cytotoxic and other biological properties.[7] Many approaches to 6*H*-dibenzo[*b*,*d*]pyran-6-ones have been developed.[8] These methods include (1) copper-catalyzed condensation of 2-bromobenzoic acids with phenols (the Hurtley reaction) and related processes[9] (2) oxidative and other cyclizations of biphenyl-2-carboxylic acids[10] (3) photochemical, thermal, transition metal and acid mediated cyclizations of 2'-substituted biphenyl-2-carboxylic acids[11] (4) Bayer-Villiger oxidation of 9-fluorenones[12] (5) biomimetic cyclization of polyketides[13] (6) Pechmann condensation-oxidation sequences[14] (7) elaboration of coumarins using cycloaddition-oxidation sequences[15] and (8) acid and base mediated rearrangements of spiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3-ones.[16,17] Due in part to our interest in the gilvocarcin family of antitumor antibiotics, we have examined the last of these methods of 6*H*-dibenzo[*b*,*d*]pyran-6-one synthesis in some detail.[18] These studies have revealed new conditions for conducting this transformation and our results are reported here.

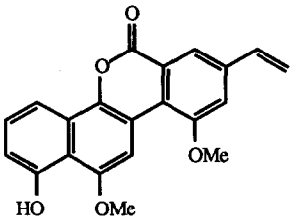
Nearly thirty years ago Hey, Leonard and Rees reported that treatment of spirodienone **8** with 15% aqueous sulfuric acid at reflux afforded dibenzopyranone **4** in 80% yield.[16] They also showed that treatment of **8** with 10% aqueous sodium hydroxide at reflux gave an isomeric dibenzopyranone **4** in 70% yield. It was proposed that these isomers were formed by dienone-phenol type rearrangements that involved formal O-migration (**8** → **4**) and C-migration (**8** → **9**), respectively.[19]



1 $R_1 = R_7 = H$ $R_3 = R_9 = R_{10} = OH$
2 $R_1 = Me$ $R_{10} = H$ $R_3 = R_7 = R_9 = OH$
3 $R_1 = Me$ $R_9 = R_{10} = H$ $R_3 = R_7 = OH$
4 $R_1 = R_7 = R_9 = R_{10} = H$ $R_3 = OH$
5 $R_1 = R_7 = R_9 = R_{10} = H$ $R_3 = OMe$



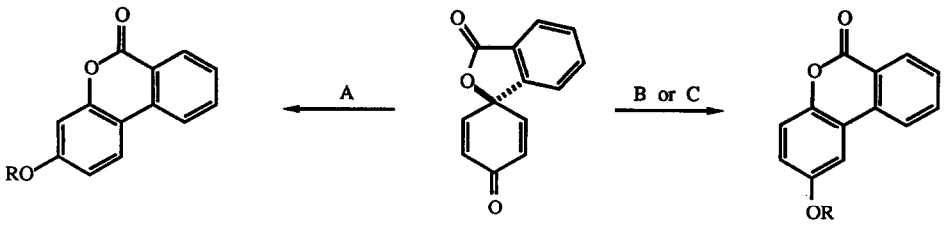
6



7

We began our studies with a reexamination of these reactions as shown below. Spirodienone **8** was prepared in 52% yield by sequential treatment of *N*-phenylbenzamide with two equivalents of *n*-butyllithium and an excess of 4,4-dimethoxycyclohexadienone,[20] followed by an aqueous hydrochloric acid work-up. We were able to reproduce the results of the Hey group without difficulty. Thus, treatment of **8** with 50% aqueous sulfuric acid at reflux for 2 h, followed by methylation of the crude reaction mixture (potassium carbonate and dimethyl sulfate in acetone at reflux) gave phenolic ether **5** in 88% yield (condition A). In our hands, treatment of **8** with 10% aqueous sodium hydroxide at reflux for 1.5 h, followed by methylation of the crude product, gave a 95:5 mixture of the C-migration product **10** and the O-migration product **5**, respectively, in 42% yield (condition B). We were surprised to find, however, that treatment of **8** with a 2:1 mixture of trifluoroacetic anhydride and trifluoroacetic acid containing a trace of sulfuric acid gave an 86% yield of C-migration product **10** after hydrolysis and methylation of the presumed intermediate trifluoroacetate (condition C). The difference in behavior of **8** under the aforementioned acidic conditions is notable. Even more remarkable was the observation that treatment of **8** with a 2:1 mixture of acetic anhydride and acetic acid containing a trace of sulfuric acid gave the O-migration product **5** (92%) after hydrolysis and methylation of the crude mixture of products. Thus, the rearrangement path followed by **8** is very sensitive to reaction conditions. Although no mechanistic studies were performed, it is probable that the formal O-migration products result from sequential conjugate addition of an oxygen nucleophile (water or acetic acetic acid) to dienone **8**, aromatization with elimination of the lactone oxygen, and lactonization of an intermediate 2'-hydroxybiphenyl-2-carboxylate. The rearrangement in base may involve lactone hydrolysis followed by rearrangement of an intermediate 4-oxido-4-arylcyclohexadienone as previously suggested by Hey.[16] The difference between the acetic acid and trifluoroacetic acid mediated rearrangements may be related to the difference in nucleophilicities of acetate and trifluoroacetate as well as relative acid strengths.

We next examined the series of substituted spirodienones (**11a-11e**) shown in Figure 1. With the exception of **11d**, the spirodienones were prepared from 4,4-dimethoxycyclohexadienone and the lithium dianions derived from appropriately substituted benzamides (**14**) in the yields indicated below structure **11**.[21,22] The aryllithium derived from metallation of oxazoline **15** ($R_8 = R_9 = H$ and $R_{10} = Cl$) provided a superior yield of **11d**.

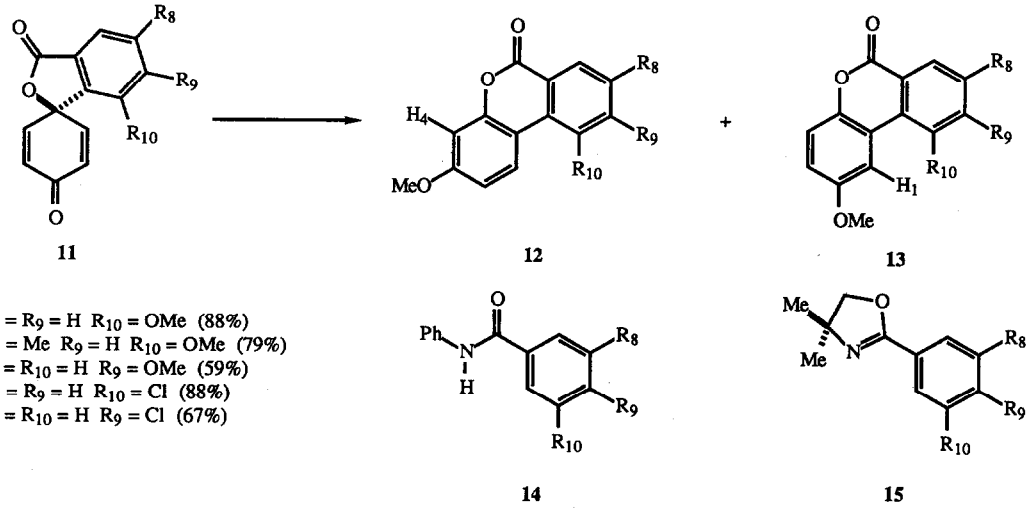


4 R = H **5** R = Me **8** **9** R = H **10** R = Me

(A) 1. 50% aqueous H_2SO_4, Δ 2. K_2CO_3, Me_2SO_4 (B) 1. 10% aqueous NaOH, Δ 2. K_2CO_3, Me_2SO_4
(C) 1. $(CF_3CO)_2O$–CF_3CO_2H-H_2SO_4, Δ 2. K_2CO_3, MeOH 3. K_2CO_3, Me_2SO_4

The results of a series of rearrangement studies are documented in Table 1. Each substrate was subjected to the three rearrangement conditions mentioned above. The structures of the products (**12** and **13**) were assigned on the basis of spectroscopic data. The chemical shifts of H_4 in **12** and H_1 in **13** clearly distinguished between the formal O-migration and C-migration products. For example, H_4 always appeared as doublet (J = 2-3 Hz) in the δ 6.6-6.9 chemical shift range while H_1 (**13**) appeared as a doublet (J = 2-3 Hz) at about δ 7.4 for **5**, **13c** and **13e** and at about δ 8.5 for **13a** and **13b**. The downfield shift of H_1 in **13** is indicative of the sterically conjested environment of this proton.

Figure 1



11 **12** **13**

a $R_8 = R_9 = H$ $R_{10} = OMe$ (88%)
b $R_8 = Me$ $R_9 = H$ $R_{10} = OMe$ (79%)
c $R_8 = R_{10} = H$ $R_9 = OMe$ (59%)
d $R_8 = R_9 = H$ $R_{10} = Cl$ (88%)
e $R_8 = R_{10} = H$ $R_9 = Cl$ (67%)

14 **15**

The results indicate that rearrangements in aqueous sulfuric acid (entries 1, 4, 7, 10, 13, 16) consistently afford high yields of the formal O-migration product. Rearrangements using aqueous sodium hydroxide (entries 2, 5, 8, 11, 14, 17) are unpredictable and usually proceed in low yield. Rearrangements in trifluoroacetic anhydride-trifluoroacetic acid-sulfuric acid consistently give rise to good yields of C-migration products (entries

3, 6, 9, 12) if the migrating aryl ring is unsubstituted or carries electron-donating substituents. Placement of an inductive electron-withdrawing group on the aryl ring, however, slows the rate of aryl migration relative to formal O-migration. For example, spirodienone **11e** gives a 1:1 mixture of **12e**:**13e** while spirodienone **11d**, where the chloro group is closer to the migrating center, affords only **12d**.

Table1. Acid and Base Mediated Rearrangements of Spirodienones 8 and 11

Entry	Substrate	Conditions[a]	O-Migration (12)[b]	C-Migration (13)[b]	%Yield[c]
1	**8**	A	100	—	88
2	**8**	B	5	95	42[d]
3	**8**	C	—	100	86
4	**11a**	A	100	—	86[e]
5	**11a**	B	50	50	38[d,f]
6	**11a**	C	—	100	78[e]
7	**11b**	A	100	—	79[e]
8	**11b**	B	100	—	26
9	**11b**	C	—	100	86[e]
10	**11c**	A	100	—	54
11	**11c**	B	—	—	0
12	**11c**	C	—	100	61
13	**11d**	A	100	—	60
14	**11d**	B	100	—	2
15	**11d**	C	100	—	30
16	**11e**	A	100	—	70
17	**11e**	B	—	—	0
18	**11e**	C	50	50	55[d]

a. Condition A = 1. 50% aqueous H_2SO_4, Δ 2. K_2CO_3, Me_2SO_4; Condition B = 1. 10% aqueous NaOH, Δ 2. K_2CO_3, Me_2SO_4; Condition C = 1. $(CF_3CO)_2O$-CF_3CO_2H-H_2SO_4, Δ 2. K_2CO_3, MeOH 3. K_2CO_3, Me_2SO_4.

b. Instances where no O-migration or C-migration product were detected are indicated by a dash. The O-migration and C-migration products were **5** and **10**, respectively in entries 1-3.

c. Yield of product after purification.

d. Yield of purified mixture of products. Product ratios were determined by ^1H NMR.

e. The phenolic product produced in the dienone-phenol rearrangement was also isolated and characterized as described in the experimental section.

f. It is notable that treatment of **11a** with 6% methanolic potassium methoxide gave 4'-hydroxy-2',6-dimethoxybiphenyl-2-carboxylic acid in 78% yield (mp 228°C).

In summary, the dienone-phenol rearrangement route to 6*H*-dibenzo[*b*,*d*]pyran-6-ones has been extended. More general conditions for accomplishing C-migration have been uncovered. Electronic effects on the relative rates of formal O-migration and C-migration have been examined and, although numerous systems have not been studied, it appears that migration of electron rich aryl groups are more general than migration of electron deficient aryl groups. We imagine that this methodology will be suitable for the synthesis of several of the natural products described in the introduction.

Experimental

General Information: All melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H Nuclear magnetic resonance spectra were recorded on Bruker AM-250 or Bruker AM-300 spectrometers and are reported in parts per million from internal tetramethylsilane on the δ scale. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (in hertz), integration, interpretation]. ^{13}C Nuclear magnetic resonance spectra were recorded on the aforementioned instruments and are reported in parts per million from internal tetramethylsilane as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet)]. Multiplicities were obtained from DEPT or INEPT spectra. Column chromatography was performed over EM Laboratories silica gel 60 (230-400 mesh). Oxazoline **15d**[23] and amides **14a**,[24] **14b**,[25] **14c**[26] and **14e**[27] are known compounds and were prepared by standard methods as were *N*-phenylbenzamide and 4,4-dimethoxycyclohexadien-one.[20]

Preparation of a Spirodienone: Spiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'-one (8). To a solution of 2 g (11 mmol) of *N*-phenylbenzamide in 20 mL of tetrahydrofuran was added 17.3 mL (24.7 mmol) of *n*-butyllithium (1.43 M in hexane) slowly at -78°C under argon. The yellow solution was stirred for 0.5 h at -78°C, at 0°C for 1.5 h, and then cooled to -78°C. A solution of 2.29 g (17 mmol) of 4,4-dimethoxycyclohexadienone in 20 mL of tetrahydrofuran was added and the solution was stirred for 4 h. The mixture was diluted with 100 mL of ether and washed with three 100-mL portions of 3 N aqueous hydrochloric acid. The combined aqueous layers were extracted with three 50-mL portions of ether. The combined organic layers were washed with 100 mL of brine and dried ($MgSO_4$). The organic phase was concentrated in vacuo and the residue was recrystallized from methanol to afford 1.21 g (52%) of spirolactone **8** as white crystals: mp 181-182°C (lit 189°C)[16,28]; IR (CCl_4) 1776, 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.43 (dt, *J* =10, 3 Hz, 2H, =CH), 6.65 (dt, *J* =10, 3 Hz, 2H, =CH), 7.28 (d, *J* = 7.6 Hz, 1H, H7), 7.63 (td, *J* = 7.4, 1 Hz, 1H, H_6), 7.71 (td, *J* = 7.4, 1 Hz, 1H, H_5), 7.97 (d, *J* = 7.6 Hz, 1H, H_4); ^{13}C NMR ($CDCl_3$) δ 80.4 (s), 122.4 (d), 125.7 (s) 126.8 (d), 129.9 (d), 130.7 (d), 135.1 (d), 144.3 (d), 146.6 (s), 168.9 (s), 184.2 (s); exact mass calcd. for $C_{13}H_8O_3$ *m/e* 212.0474, found *m/e* 212.0470. Anal. calcd. for $C_{13}H_8O_3$: C, 73.59; H, 3.77. Found: C, 73.35; H, 3.83.

7'-Methoxyspiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'one (11a). This spirodienone was prepared from *N*-phenyl-3-methoxybenzamide (**14a**) (8.81 mmol) and 4,4-dimethoxycyclohexadienone (14.1 mmol) in 88% yield. Purification of the crude product was accomplished by chromatography over 100 g of silica gel (ethyl acetate-hexane, 1:2): mp 153-155°C; IR ($CHCl_3$) 1775, 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H, OCH_3), 6.41 (d, *J* = 10 Hz, 2H, =CH), 6.51 (d, *J* = 10 Hz, 2H, =CH), 7.11 (dd, *J* = 7, 2 Hz, 1H, H_6), 7.57 (m, 2H, H_4 and H_5); ^{13}C NMR ($CDCl_3$) δ 55.8 (q), 79.1 (s), 116.3 (d), 117.9 (d), 127.6 (s), 130.44 (d), 132.7 (d), 133.1 (s), 142.5 (d), 154.7 (s), 168.9 (s), 184.6 (s); exact mass calcd for $C_{14}H_{10}O_4$ *m/e* 242.0579, found *m/e* 242.0581. Anal. calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16. Found: C, 69.39; H, 4.13.

7'-Methoxy-5'-methylspiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'one (11b). This spirodien-one was prepared from *N*-phenyl-3-methoxy-5-methylbenzamide (**14b**) (1.24 mmol) and 4,4-dimethoxycyclohexadienone (2.6 mmol) in 79% yield. Purification of the crude product was accomplished by chromatography over 100 g of silica gel (ethyl acetate-hexane, 1:3): mp 190-193°C; IR (CH_2Cl_2) 1780, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 6.35 (d, *J* = 10.1 Hz, 2H, =CH), 6.5 (d, *J* = 10.1 Hz, 2H, =CH), 6.9 (s, 1H, H_6), 7.3 (s, 1H, H_4); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 55.7 (q), 78.9 (s), 117.4 (d), 118.0 (d), 127.6 (s), 130.2 (d), 130.4 (s), 142.8 (d), 143.7 (s), 154.3 (s), 169.0 (s), 184.7 (s); exact mass calcd for $C_{15}H_{12}O_4$ *m/e* 256.0736, found *m/e* 256.0717. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.25; H, 4.82.

6'-Methoxyspiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-3'-one (11c). This spirodienone was prepared from *N*-phenyl-4-methoxybenzamide (**14c**) (3.5 mmol) and 4,4-dimethyoxyyclohexadienone (5.2 mmol) in 59% yield. Purification of the crude product was accomplished by recrystallization from methanol-acetone-ether: mp 193-196°C; IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.8 (s, 3H, OCH_3), 6.4 (d, *J* =

10 Hz, 2H, =CH), 6.65 (d, J = 10 Hz, 2H =CH), 6.65 (d, J = 2.1 Hz, 1H, H7), 7.1 (dd, J = 8.5, 2.1 Hz, 1H, H5), 7.85 (d, J = 8.5 Hz, 1H, H4); ^{13}C NMR ($CDCl_3$) δ 56.1 (q), 79.6 (s), 105.9 (d), 117.7 (s), 118.3 (d), 128.2 (d), 129.8 (d), 144.5 (d), 149.5 (s), 165.5 (s), 168.6 (s), 184.3 (s); exact mass calcd. for $C_{14}H_{10}O_4$ *m/e* 242.0579, found *m/e* 242.0571. Anal. calcd. for $C_{14}H_{10}O$: C, 69.40; H, 4.16. Found: C, 69.32; H, 4.20.

7'-Chlorospiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran}-3'-one (11d). This spirodienone was prepared from oxazoline **15d** (4.78 mmol), *n*-BuLi (4.78 mmol), and 4,4-dimethyoxycyclohexadienone (7.2 mmol) in 88% yield. Purification of the crude product was accomplished by recrystallization from methanol-water: mp 175-175.5°C; IR ($CHCl_3$) 1781 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 6.5 (s, 4H, CH=CH), 7.58-7.64 (m, 2H, H5 and H6), 7.9 (dd, J = 7.2, 1.4 Hz, 1H, H4); ^{13}C NMR ($CDCl_3$) δ 79.5 (s), 125.2 (d), 128.3 (s), 130.0 (s), 131.9 (d), 132.4 (d), 136.0 (d), 140.7 (d), 142.3 (s), 167.5 (s), 184.1 (s); exact mass calcd. for $C_{13}H_7ClO_3$ *m/e* 246.0083, found *m/e* 246.0086. Anal. calcd. for $C_{13}H_7ClO_3$: C, 63.41; H, 2.85. Found: C, 63.72; H, 3.03.

6'-Chlorospiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran}-3'-one (11e). This spirodienone was prepared from *N*-phenyl-4-chlorobenzamide (**14e**) (4.3 mmol) and 4,4-dimethyoxycyclohexadienone (6.5 mmol) in 67% yield. Purification of the crude product was accomplished by recrystallization from acetone-water: mp 157-158°C; IR (CCl_4) 1790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.4 (d, J = 10.1 Hz, 2H, =CH), 6.5 (d, J = 10.1 Hz, 2H, =CH), 7.2 (d, J = 1.6 Hz, 1H, H7), 7.6 (dd, J = 8.2, 1.6 Hz, 1H, H5), 7.9 (d, J = 8.2 Hz, 1H, H4); ^{13}C NMR ($CDCl_3$) δ 79.8 (s), 122.9 (d), 124.1 (s), 127.9 (d), 130.3 (d), 131.5 (d), 142.0 (s), 143.4 (d), 148.3 (s), 167.7 (s), 183.8 (s); exact mass calcd. for $C_{13}H_7ClO_3$ *m/e* 246.0083, found *m/e* 246.0040. Anal. calcd. for $C_{13}H_7ClO_3$: C, 63.41; H, 2.85. Found: C, 63.38; H, 2.88.

Spirodienone Rearrangement Using Aqueous Sulfuric Acid (Condition A): 3-Methoxy-6*H*-dibenzo[*b,d*]pyran-6-one (5). A mixture of 100 mg (0.47 mmol) of spirolactone **8** in 5 mL of 50% aqueous sulfuric acid was refluxed for 2 h. The milky white mixture was cooled to room temperature, diluted with 50 mL of water, and 50 mL of saturated aqueous sodium bicarbonate was added slowly. The mixture was extracted with three 50-mL portions of ethyl acetate and the combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in 5 mL of acetone followed by addition of 324 mg (2.35 mmol) of potassium carbonate and 296 mg (2.35 mmol) of dimethyl sulfate. The mixture was warmed under reflux for 16 h, diluted with 10 mL dichloromethane, and filtered. The filtrate was washed with three 25-mL portions of 10% aqueous citric acid and the aqueous washes were extracted with 25 mL of dichloromethane. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was crystallized from acetone-hexane to afford 94 mg (88%) of dibenzopyranone **5** as white crystals: mp 144-148°C (lit 140-144°C)[3,29]; IR (CCl_4) 1724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.9 (s, 3H, OCH_3), 6.88 (d, J = 2.5 Hz, 1H, H4), 6.92 (dd, J = 8.7, 2.5 Hz, 1H, H2), 7.5 (t, J = 7.5 Hz, 1H, H8), 7.8 (td, J = 7.5, 1.4 Hz, 1H, H9), 7.95 (d, J = 8.7 Hz, 1H, H1), 8.02 (d, J = 7.5 Hz, 1H, H10), 8.38 (dd, J = 7.5, 1.0 Hz, 1H, H7); ^{13}C NMR ($CDCl_3$) δ 55.67 (q), 101.63 (d), 111.15 (s), 112.43 (d), 119.99 (s),121.04 (d), 123.75 (d), 127.70 (d),130.55 (d), 134.83 (d), 135.17 (s), 152.63 (s), 161.46 (s), 161.49 (s); exact mass calcd. for $C_{14}H_{10}O_3$ *m/e* 226.0629, found *m/e* 226.0618. Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.43. Found: C, 73.77; H, 4.44.

Spirodienone Rearrangement Using Aqueous Sodium Hydroxide (Condition B): 2-Methoxy-6*H*-dibenzo[*b,d*]pyran-6-one (10). A mixture of 100 mg (0.47 mmol) of spirolactone **8** in 3 mL of 10% sodium hydroxide was warmed under reflux for 1.5 h. The mixture was neutralized with 5 mL of 10% aqueous hydrochloric acid and extracted with three 25-mL portions of dichloromethane. The combined organic layers were washed with two 50-mL portions of saturated aqueous sodium bicarbonate, dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in 2 mL of acetone, 324 mg (2.35 mmol) of potassium carbonate and 296 mg (2.35 mmol) of dimethyl sulfate were added, and the mixture was warmed under reflux for 1 h. The mixture was diluted with 20 mL of dichloromethane and filtered. The filtrate was washed with 150 mL of 10% aqueous citric acid, dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed over 10 g of silica gel (hexane-ethyl acetate, 1:10) to give 21 mg (42%) of a 19:1 mixture of dibenzopyranone **10** (*vide infra*) and dibenzopyranone **5** (*vide supra*) as a white solid (mp 111-114°C). The ratio of isomers **10** and **5** was determined by integration of appropriate peaks in the ^{1}H NMR spectrum of the mixture.

Spirodienone Rearrangement Using Trifluoroacetic Anhydride-Trifluoroacetic Acid-Sulfuric Acid (Condition C): 2-Methoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (10). A mixture of 100 mg (0.47 mmol) of spirolactone **8**, 1 mL of trifluoroacetic acid, 2 mL of trifluoroacetic anhydride and 2 drops of concentrated sulfuric acid was warmed under reflux for 4.5 h. The solution was concentrated in vacuo and the brown residue was dissolved in 3 mL of methanol and 500 mg of potassium carbonate was added. The mixture was partitioned between 200 mL of dichloromethane and 150 mL of water. The aqueous phase was extracted with three 100-mL portions of dichloromethane. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The residue was dissolved in 10 mL of acetone and 323 mg (2.35 mmol) of potassium carbonate and 296 mg (2.35 mmol) of dimethyl sulfate were added. The solution was warmed under reflux for 3 h, diluted with 10 mL of dichloromethane and filtered. The filtrate was dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed over 10 g of silica gel (ethyl acetate-hexanes, 1:10) followed by recrystallization from methanol-water to afford 92 mg (86%) of dibenzopyranone **5** as a white solid: mp 118-119°C (lit 119-123°C)[30]; IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (s, 3H, OCH_3), 7.02 (dd, J = 9, 2.9 Hz, 1H, H_3), 7.27 (d, J = 9.0, 1H, H_4), 7.47 (d, J = 2.9 Hz, 1H, H_1) 7.57 (td, J = 7.4, 1.0 Hz, 1H, H_8), 7.80 (td, J = 7.4, 1.4 Hz, 1H, H_9), 8.04 (d, J = 8.1 Hz, 1H, H_{10}), 8.40 (dt, J = 7.4, 1.0 Hz, 1H, H_7); ^{13}C NMR ($CDCl_3$) δ 55.8 (q), 106.3 (d), 117.1 (d), 118.5 (s), 118.6 (d), 121.3 (s), 121.6 (d), 128.9 (d), 130.6 (d), 134.6 (s), 134.7 (d), 145.5 (s), 156.3 (s), 161.3 (s); exact mass calcd. for $C_{14}H_{10}O_3$ *m/e* 226.0629, found *m/e* 226.0630.

3,10-Dimethoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (12a). This compound was obtained from **11a** (0.83 mmol) in 86% yield using condition A described above. The crude product was purified by recrystallization from ethyl acetate-hexane: mp 158-160°C; IR (CH_2Cl_2) 1727 cm^{-1}; ^1H NMR (C_6D_6) δ 3.20, (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3), 6.55 (dd, J = 10, 1 Hz, 1H, H_9), 6.7 (d, J = 2.5 Hz, 1H, H_4), 6.85 (dd, J = 10, 2.5 Hz, 1H, H_2), 6.95 (t, J = 10 Hz, 1H, H_8), 8.25 (dd, J = 10, 1 Hz, 1H, H_7), 8.9 (d, J = 10 Hz, 1H, H_1); ^{13}C NMR ($CDCl_3$) δ 55.5 (q), 55.9 (q), 101.3 (d), 110.8 (s), 111.5 (d), 116.6 (d), 121.8 (s), 122.5 (d), 124.5 (s), 127.9 (d), 129.5 (d), 152.2 (s), 156.5 (s), 160.5 (s), 161.5 (s); exact mass calcd for $C_{15}H_{12}O_4$ *m/e* 256.0736; found, *m/e* 256.0754. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.14; H, 4.78. In this case the intermediate phenol (3-hydroxy-10-methoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one) was isolated in 97% yield and characterized as follows: IR (CH_2Cl_2) 3000, 1728 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.85 (br s, 1H, OH), 4.10 (s, 3H), 6.78 (d, J = 1.5 Hz, 1H, H_4), 6.9 (dd, J = 10, 1.5 Hz, 1H, H_2), 7.53 (m, 2H, ArH), 7.95 (m, 1H, ArH), 8.85 (d, J = 10 Hz, 1H, H_1); ^{13}C NMR (acetone-d_6) δ 56.5 (q), 103.8 (d), 110.7 (s), 113.1 (d), 117.2 (d), 122.5 (s), 122.8 (d), 125.2 (s), 128.8 (d), 130.8 (d), 153.3 (s), 157.6 (s), 159.6 (s), 161.3 (s); exact mass calcd for $C_{14}H_{10}O_4$ *m/e* 242.0579; found, *m/e* 242.0586.

2,10-Dimethoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one (13a). This compound was obtained from **11a** (0.83 mmol) in 78% yield using condition C described above: mp 170-171°C; IR (CH_2Cl_2) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 6.9 (dd, J = 9, 3 Hz, 1H, H_3), 7.2-7.4 (m, 2H, H_4 and H_9), 7.5 (t, J = 8.1 Hz, 1H, H_8), 8.0 (d, J = 8 Hz, 1H, H_7), 8.47 (d, J = 3 Hz, 1H, H_1); ^{13}C NMR ($CDCl_3$) δ 55.6 (q), 56.0 (q), 112.6 (d), 115.6 (d), 116.6 (d), 117.5 (d), 118.1 (s), 122.5 (d), 123.1 (s), 123.6 (s), 129.1 (d), 144.9 (s), 155.6 (s), 157.2 (s), 161.3 (s); exact mass calcd for $C_{15}H_{12}O_4$ *m/e* 256.0736; found, *m/e* 256.0729. In one experiment, the intermediate phenol (2-hydroxy-10-methoxy-6*H*-dibenzo[*b*,*d*]pyran-6-one) was isolated in 85% yield and characterized as follows: mp 238°C; IR (CH_2Cl_2) 3310, 1720 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.04 (s, 3H, OCH_3), 6.9 (dd, J = 8.8, 2.9 Hz, 1H, H_3), 7.2 (d, J = 8.8 Hz, 1H, H_4), 7.5-7.8 (m, 2H, H_8 and H_9), 7.89 (dd, J = 6.7, 2.3 Hz, 1H, H_7), 8.37 (d, J = 2.9 Hz, 1H, H_1), 9.51 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 56.3 (q), 113.6 (d), 117.1 (d), 117.3 (d), 117.5 (d), 117.7 (d), 121.7 (d), 122.3 (s), 122.8 (s), 129.6 (d), 143.3 (s), 153.5 (s), 175.0 (s), 160.3 (s); exact mass calcd for $C_{14}H_{10}O_4$ *m/e* 242.0579, found *m/e* 242.0576. Anal. calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16. Found: C, 69.16; H, 4.18.

3,10-Dimethoxy-8-methyl-6*H*-dibenzo[*b*,*d*]pyran-6-one (12b). This compound was obtained from **11b** (1.95 mmol) in 79% yield using condition A described above. The crude product was purified by recrystallization from acetone-methanol-water: mp 173.5-174.5°C; IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (C_6D_6) δ 3.16 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3) 6.4 (m, 1H, H_9), 6.6 (d, J = 2.5 Hz, 1H, H_4), 6.8 (dd, J = 7.5,

2.5 Hz, 1H, H_2), 8.05 (m, 1H, H_7), 8.7 (d, J = 7.5, 1H, H_1); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 55.5 (q), 55.8 (q), 101.3 (d), 111.0 (s) 111.4 (d), 117.8 (d), 121.4 (s), 121.9 (s), 122.4 (d), 129.1 (d), 138.3 (s), 151.8 (s), 156.5 (s), 160.1 (s), 161.6 (s); exact mass calcd. for $C_{16}H_{14}O_4$ *m/e* 270.0892, found *m/e* 270.0901.

2,10-Dimethoxy-8-methyl-6*H*-dibenzo[*b,d*]pyran-6-one (13b). This compound was obtained from **11b** (0.31 mmol) in 86% yield using condition C described above: mp 144-145°C; IR (CH_2Cl_2) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5 (s, 3H, CH_3), 3.9 (s, 3H, OCH_3), 4.1 (s, 3H, OCH_3), 7.0 (dd, J = 10, 2 Hz, 1H, H_3), 7.15 (s, 1H, H_7), 7.3 (d, J = 10 Hz, 1H, H_4), 7.95 (s, 1H, H_9), 8.5 (d, J = 2 Hz, 1H, H_1); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 55.6 (q), 55.9 (q), 112.4 (d), 115.1 (d), 117.5 (d), 117.8 (d), 118.3 (d), 121.2 (s), 122.7 (d), 122.8 (s), 139.8 (s), 144.7 (s), 155.7 (s), 157.2 (s), 161.5 (s); exact mass calcd for $C_{16}H_{14}O_4$: *m/e* 270.0892; found, *m/e* 270.0896. In one experiment, the intermediate phenol (2-hydroxy-10-methoxy-8-methyl-6*H*-dibenzo[*b,d*]pyran-6-one) was isolated in 87% yield and characterized as follows: mp 240-243°C (dec); ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 4.00 (s, 3H, OCH_3), 6.9 (dd J = 8.8, 2.8 Hz, 1H, H_3), 7.1 (d, J = 8.8 Hz, 1H, H_4), 7.36 (s, 1H, H_9), 7.66 (s, 1H, H_7), 8.3 (d, J = 2.8 Hz, 1H, H_1), 9.54 (s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 21.00 (q), 56.1 (q), 113.2 (d), 116.5 (d), 117.1 (d), 117.6 (s), 118.6 (d), 120.3 (s), 121.6 (d), 122.0 (s), 139.8 (s), 143.0 (s), 153.6 (s), 156.9 (s), 160.3 (s); exact mass calcd for $C_{15}H_{12}O_4$ *m/e* 156.0736, found *m/e* 256.0736.

3,9-Dimethoxy-6*H*-dibenzo[*b,d*]pyran-6-one (12c). This compound was obtained from **11c** (0.62 mmol) in 54% yield using condition A described above. The crude product was purified by recrystallization from acetone-methanol-ether: mp 188.5-191°C; IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 6.84 (d, J = 2.4 Hz, 1H, H_4), 6.88 (dd, J = 6.2, 2.7 Hz, 1H, H_2), 7.04 (dd, J = 7.4, 2.4 Hz, 1H, H_8), 7.35 (d, J = 2.4 Hz, 1H, H_{10}), 7.8 (d, J = 9.8 Hz, 1H, H_1), 8.3 (d, J = 9.6 Hz, 1H, H_7); ^{13}C NMR ($CDCl_3$) δ 55.7 (q, two carbons), 101.6 (d), 104.4 (d), 111.1 (s), 112.3 (d), 113.2 (s), 115.2 (d), 123.7 (d), 132.9 (d), 137.3 (s), 153.0 (s), 161.2 (s), 161.6 (s), 164.9 (s); exact mass calcd. for $C_{15}H_{12}O_4$ *m/e* 256.0736, found *m/e* 256.0733. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.68. Found: C, 70.38; H, 4.72.

2,9-Dimethoxy-6*H*-dibenzo[*b,d*]pyran-6-one (13c). This compound was obtained from **11c** (0.83 mmol) in 61% yield using condition C described above. The crude product was purified by recrystallization from acetone-methanol: mp 153-156°C; IR ($CHCl_3$) 1717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.9 (s, 3H, OCH_3), 4.0 (s, 3H, OCH_3), 7.05 (dd, J = 9, 2.9 Hz, 1H, H_2), 7.1 (dd, J = 9, 2.4 Hz, 1H, H_8), 7.26 (d, J = 9 Hz, 1H, H_1), 7.4 (m, 2H, H_4 and H_{10}), 8.35 (d, J = 9 Hz, 1H, H_7); ^{13}C NMR ($CDCl_3$) δ 55.7 (q), 55.9 (q), 105.3 (d), 106.5 (d), 114.4 (s), 116.0 (d), 117.1 (d), 118.5 (s), 118.7 (d), 133.0 (d), 136.7 (s), 146.0 (s), 156.2 (s), 161.1 (s), 164.8 (s); exact mass calcd. for $C_{15}H_{12}O_4$ *m/e* 256.0736, found *m/e* 256.0738.

10-Chloro-3-methoxy-6*H*-dibenzo[*b,d*]pyran-6-one (12d). This compound was obtained from **11d** (0.41 mmol) in 60% yield using condition A described above. The crude product was purified by recrystallization from methanol: mp 179-179.5 °C; IR ($CHCl_3$) 1729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.0 (s, 3H, OCH_3), 6.9 (m, 2H, H_2 and H_4), 7.4 (t, J = 8 Hz, 1H, H_8), 7.8 (dd, J = 8, 1.5 Hz, 1H , H_9), 8.4 (dd, J = 8, 1.5 Hz, 1H , H_7), 9.2 (d, J = 8.7 Hz, 1H, H_1), ; ^{13}C NMR ($CDCl_3$) δ 55.7 (q), 101.9 (d), 110.4 (s), 111.5 (d), 123.0 (s), 127.7 (d), 123.3 (d), 130.0 (s), 130.1 (d), 132.1 (s), 138.4 (d), 152.8 (s), 160.6 (s), 161.5 (s); exact mass calcd. for $C_{14}H_9ClO_3$ *m/e* 260.0240, found *m/e* 260.0263. Anal. calcd. for $C_{14}H_9ClO_3$: C, 64.46; H, 3.46. Found: C, 64.34; H, 3.51. Dibenzopyranone **12d** was obtained from **11d** (0.41 mmol) in 30% yield using condition C described above and acetone-water as the recrystallization solvent (mp 176-177°C).

9-Chloro-3-methoxy-6*H*-dibenzo[*b,d*]pyran-6-one (12e). This compound was obtained from **11e** (0.82 mmol) in 70% yield using condition A described above. The crude product was purified by recrystallization from methanol-water: mp 187.5-188°C; IR (CCl_4) 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.9 (s, 3H, OCH_3), 6.8 (d, J = 2.5 Hz, 1H, H_4), 6.9 (dd, J = 8, 2.5 Hz, 1H, H_2) 7.4 (dd, J = 8.5, 2 Hz, 1H, H_8), 7.8 (d, J = 8 Hz, 1H, H_1), 7.9 (d, J = 2 Hz, 1H, H_{10}), 8.2 (d, J = 8.5 Hz, 1H, H_7); ^{13}C NMR ($CDCl_3$) δ 55.7 (q), 101.7 (d), 110.1 (s), 112.7 (d), 118.3 (s), 121.1 (d), 123.9 (d), 128.1 (d), 132.2 (d), 136.7 (s), 141.8 (s), 153.0 (s), 160.7 (s), 162.1 (s); exact mass calcd. for $C_{14}H_9ClO_3$ *m/e* 260.0240, found *m/e*

260.0260. Anal. calcd. for $C_{14}H_9ClO_3$: C, 64.46; H, 3.46. Found: C, 63.80; H, 3.40. Rearrangement of **11e** (0.41 mmol) using conditions C described above gave a 55% yield of a 1:1 mixture of **12e** and **13e**. Attempts to separate **12e** and **13e** failed, but diagnostic peaks for **13e** were detected in the ^1H NMR ($CDCl_3$) spectrum of the mixture: δ 3.8 (s, 3H, OCH_3), 7.1 (dd, J = 9.0, 2.9 Hz, 1H, H_2), 7.3 (d, J = 9.0 Hz, 1H, H_4), 7.4 (d, J = 2.9 Hz, 1H, H_1), 7.55 (dd, J = 8.5, 1.2 Hz, 1H, H_8), 8.02 (d, J = 1.2 Hz, 1H, H_7), 8.33 (d, J = 8.5 Hz, 1H, H_{10}).

References and Notes

1. Heerden, F. R.; Brandt, E. V.; Ferreira, D.; Roux, D. G. *J. Chem. Soc. Perkin 1* **1981**, 2483. Burger, A. P. N.; Brandt, E. V.; Roux, D. G. *Phytochemistry* **1983**, *22*, 2813. Young, D. A.; Ferreira, D.; Roux, D. G. *J. Chem. Soc. Perkin Trans. 1* **1983**, 2031.
2. Sidwell, W. T. L.; Fritz, H.; Tamm, Ch. *Helv. Chem. Acta* **1971**, *54*, 207.
3. Ghosal, S.; Reddy, J. P.; Lal, V. K. *J. Pharm. Sci.* **1976**, *65*, 772.
4. Lederer, E.; Polonsky, J. *Bull Soc. Chim. Fr.* **1948**, 831. Lederer, E. *J. Chem. Soc.* **1949**, 2115.
5. Adams, R.; Pease, D. C.; Clark, J. H.; Baker, B. R. *J. Am. Chem. Soc.* **1940**, *62*, 2197. Ghosh, R.; Todd, A. R.; Wilkinson, S. *J. Chem. Soc.* **1940**, 1393. Novak, J.; Salemink, C. A. *J. Chem. Soc. Perkin Trans. 1* **1983**, 2867, 2873.
6. Misra, R.; Tritch, H. R.; Pandey, R. C. *J. Antibiotics* **1985**, *38*, 1280.
7. Cytotoxicity: Pero, R. W.; Owens, R. G.; Dale, S. W.; Harvan, D. *Biochim. Biophys. Acta* **1971**, *230*, 170. Pero, R. W.; Harvan, D.; Blois, M. C. *Tetrahedron Lett.* **1973**, 945. Aldose reductase inhibitors: Nakayama, H.; Ishikura, M.; Ueda, Y.; Imai, K.; Terajima, M.; Akio, S. (Japanese Patent); *Chem. Abstracts* **1990**, *112*, 178673r.
8. With the exception of the dienone-phenol method, only recent examples are cited below. Most of these are post-1975 as much of the earlier literature can be found in: Devlin, J. P. *Can. J. Chem.* **1975**, *53*, 343.
9. Hurtley, W. R. H. *J. Chem. Soc.* **1929**, 1870. Cavill G. W. K.; Dean, F. M.; Keenan, J. F. E.; McGookin, A.; Robertson, A.; Smith, G. B. *J. Chem. Soc.* **1958**, 1544. Mayer, W.; Fikentscher, R. *Chem. Ber.* **1958**, *91*, 1536. Seto, S.; Sato, H. *Bull. Chem. Soc. Jpn.* **1962**, 35, 349. Chazan, J-B.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1968**, 1374. Farkas, L.; Soti, F.; Incze, M.; Nogradi, M. *Chem. Ber.* **1974**, *107*, 3874. Soti, F.; Incze, M.; Kajtar-Peredy, M.; Baitz-Gacs, E.; Imre, L.; Farkas, L. *Chem. Ber.* **1977**, *110*, 979. Benturello, C.; Chiusoli, G. P. *J. Heterocyclic Chem.* **1972**, 1155. Muller, P.; Venakis, T.; Eugster, C. H. *Helv. Chim. Acta* **1979**, *62*, 2833. Rao, B. V.; Somayajulu, V. V. *J. Indian Chem. Soc.* **1980**, *57*, 837. Manthey, M. K.; Pyne, S. G.; Truscott, J. W. *J. Org. Chem.* **1990**, *55*, 4581.
10. Edwards, R. L.; Lewis, D. G. *J. Chem. Soc.* **1959**, 3250. Bunton, C. A.; Kenner, G. W.; Robinson, M. J. T.; Webster, B. R. *Tetrahedron* **1963**, *19*, 1001. Dewar, P. S.; Forrester, A. R.; Thomson, R. H. *J. Chem. Soc. (C)* **1971**, 3950. Abramovitch, R. A.; Cooper, M.; Iyer, S.; Jeyaraman, R.; Rodriguez, J. A. R. *J. Org. Chem.* **1982**, *47*, 4820.
11. Huntress, E. H.; Seikel, M. K. *J. Am. Chem. Soc.* **1939**, *61*, 1358. Bentley, K. W.; Robinson, R. *J. Chem. Soc.* **1952**, 947. Mathur, K. B. L.; Sarbhai, K. P. *Tetrahedron Lett.* **1964**, 1743. Collington, D. M.; Hey, D. H.; Rees, C. W. *J. Chem. Soc. (C)* **1968**, 1030. Rigby, W. *J. Chem. Soc.* **1971**, 765. Shahidi, F.; Tidwell, T. T. *Can. J. Chem.* **1982**, *60*, 1092, 1098. Ames, D. E.; Opalko, A. *Tetrahedron* **1984**, *40*, 1919. Neumeister, J.; Griesbaum, K. *Chem. Ber.* **1984**, *117*, 1640. Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.* **1985**, 5997. Little, C. B.; Schuster, G. B. *J. Org. Chem.* **1986**, *51*, 2050. Sargent, M. V. *J. Chem. Soc. Perkin Trans 1* **1987**, 2553. Boye, O.; Itoh, Y.; Brossi, A. *Helv. Chim. Acta* **1989**, *72*, 1690.
12. Mehta, G.; Pandey, P. N. *Synthesis* **1975**, 404.
13. Koelsch, C. F.; Embree, H. D. *J. Org. Chem.* **1958**, *23*, 1606. Hay, J. V.; Harris, T. M. *J. Chem. Soc., Chem. Commun.* **1972**, 953. Harris, T. M.; Hay, J. V. *J. Am. Chem. Soc.* **1977**, *99*, 1631. Leeper, F. J.; Staunton, J. *J. Chem. Soc. Perkin Trans. 1* **1984**, 1053. Abell, C.; Bush, B. D.; Staunton, J. *J. Chem. Soc., Chem Commun.* **1986**, 15.
14. Adams, R.; Baker, B. R. *J. Am. Chem. Soc.* **1940**, *62*, 2401. Miyano, M.; Dorn, C. R. *J. Org. Chem.* **1972**, *37*, 259. Kraatz, U.; Korte, F. *Chem. Ber.* **1973**, *106*, 62. Chebaane, K.; Guyot, M.; Molho, D. *Bull. Soc. Chim. Fr.* **1975**, 2521.
15. Adams, R.; McPhee, W. D.; Carlin, R. B.; Wicks, Z. W. *J. Am. Chem. Soc.* **1943**, *65*, 356. Grigg, R.; Vipond, D. *Tetrahedron* **1989**, *45*, 7587.

16. Hey D. H.; Leonard, J. A.; Rees, C. W. *J. Chem. Soc.* **1963**, 5251. For related studies see Hey, D. H.; Leonard, J. A.; Moynehan, T. M.; Rees, C. W. *J. Chem. Soc.* **1961**, 233.
17. Pavlidis, V. H.; Medcalf, H.; Coutts, I. G. C. *Syn. Commun.* **1989**, *19*, 1247. This article describe the preparation of spirodienone lactones from metallated aryloxazolines and 2,6-disubstituted-*p*-benzoquinones. One relevant dienone-phenol rearrangement is described although the structure of the product (O-migration vs. C-migration) was not determined. For a relevant formal O-migration brought to our attention by a referee see Abramovitch, R. A.; Hawi A.; Rodrigues, J. A. R.; Trombetta, T. R. *J. Chem. Soc., Chem. Commn.* **1986**, 283.
18. Hart, D. J.; Merriman, G. H. *Tetrahedron Lett.* **1989**, 5093.
19. For reviews of the dienone-phenol rearrangement see Collins, C. J.; Eastham, J. D. in *Chemistry of the Carbonyl Group*, Patai, S., Ed.; Interscience : New York, (1966), p.755. Waring, A. J. *Adv. Alicyclic Chem.* **1967**, *1*, 207. Miller, B. in *Mechanisms of Molecular Migrations*, Thyagarajan, B. S., Ed.; Interscience: New York (1968), Vol. 1, p.275. Miller, B. *Accts. Chem. Res.* **1975**, *8*, 277.
20. For an excellent review on the use of quinone monoketals in synthesis see Swenton, J. S. in *The Chemistry of Quinonoid Compounds*, Patai, S.; Rappoport, Z., Ed.; Wiley: New York (1988), Vol. 2, p. 899.
21. For metallation of benzamides see Rodriguez, H. R.; Marxer, A.; McKenna, M. M.; Tsai, H. M. *J. Org. Chem.* **1975**, *40*, 1427. Hauser, C. R.; Puterbaugh, W. H. *J. Org. Chem.* **1964**, *29*, 853.
22. For metallation of **15d** see Meyers, A. I.; Rieker, W. *Tetrahedron Lett.* **1982**, 2091. Also see Gschwend, H. W.; Hamdan, A. *J. Org. Chem.* **1975**, *40*, 2008.
23. Meyers, A. I.; Gabel, R.; Mihelich, E. D. *J. Org. Chem.* **1978**, 1372.
24. Dhar, D. N.; Gupta, S. R. *Ind. J. Chem.* **1986**, *25B*, 533.
25. This amide (mp 105-106°C) was prepared from ethyl 3-methoxy-5-methylbenzoate[18] and PhNHMgBr in 73% yield.
26. Lossen, W. *Annalen* **1875**, *175*, 293. Michman, M.; Meidar, D. *J. Chem. Soc. Perkin Trans. 1* **1972**, 300.
27. Emmerling, O. *Chem. Ber.* **1875**, *8*, 880. Hantzsch, A. *Chem. Ber.* **1891**, *24*, 51.
28. Hey. D. H.; Leonard, J. A.; Rees, C. W. *J. Chem. Soc.* **1963**, 5263.
29. Cirigottis, K. A.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1974**, *27*, 2209. Glover, S. A.; Golding, S. L.; Goosen, A.; McCleland, C. W. *J. Chem. Soc. Perkin Trans. 1* **1981**, 842.
30. Cook, J. W.; Dickson, G. T.; Jack, J.; Loudon, J. D.; McKeown, J.; MacMillan, J.; Williamson, W. F. *J. Chem. Soc.* **1950**, 139. Kenner, G. W.; Murray, M. A.; Tylor, C. M. B. *Tetrahedron* **1957**, 259. Horner, L.; Baston, D. W. *Liebigs Ann. Chem.* **1973**, 910.

Acknowledgements. We thank the National Science Foundation Young Scholars Program and The National Institutes of Health for partial support. We thank Dr. Kurt Loening for help with nomenclature and The Ohio State University Campus Chemical Instrumentation Center for use of NMR and mass spectrometers.