Table I. Acetalization and Allylation of Carbonyl Compounds

entry	alkoxysilane	carbonyl compound	conditions[a]	product (% yield)[b]
1	$(MeO)_4Si$ (**3a**)	PhCHO (**2a**)	−78°, 3 h; then rt, 4 h	$PhCH(OMe)_2$ (**4a**) (87)
2	**3a**[c]	**2a**	−30 °C, 6 h; then rt, 3 h	$PhCH(OMe)CH_2CH{=}CH_2$ (**7a**) (90)
3	**3a**	$CH_3(CH_2)_2CHO$	−40 °C, 1 h; then 0 °C, 15 min	$CH_3(CH_2)_2CH(OMe)_2$ (**4b**) (91)
4	**3a**[c]	$CH_3(CH_2)_4CHO$	−78 °C, 15 min; then 0 °C, 3 h	$CH_3(CH_2)_4CH(OMe)CH_2CH{=}CH_2$ (**7b**) (94)
5	**3a**[c]	$CH_3(CH_2)_2CH(CH_3)CHO$	−40 °C, 30 min; then 0 °C, 4 h	$CH_3(CH_2)_2CH(CH_3)CH(OMe)CH_2CH{=}CH_2$ (**7c**) (77)
6	$Me_3SiO(CH_2)_4OSiMe_3$ (**3b**)	2-cyclohexenone (**2b**)	−78 °C, 5 h	1,4-dioxaspiro[4.5]dec-7-ene (**4c**) (86)
7	**3a**[c]	**2b**	−40 °C, 30 min; then 0 °C, 4 h	1-methoxy-1-allylcyclohexa-2,5-diene (**7d**) (90)

[a] All reactions were carried out in dichloromethane in the presence of a catalytic amount of iodotrimethylsilane. [b] Yields after isolation by TLC. [c] A small excess amount (1.2 equiv) of **6** was added. rt = room temperature.

Cyclohexanone ethylene acetal (4c):[11] TLC (PhH/Hex, 2/3) R_f 0.4; NMR (CCl_4) δ 1.50 (s, 10 H), 3.85 (s, 4 H).

4-Methoxy-4-phenyl-1-butene (7a):[12] TLC (PhH/Hex, 1/1) R_f 0.5; NMR (CCl_4) δ 2.15–2.73 (m, 2 H), 3.15 (s, 3 H), 4.03 (t, J = 6 Hz, 1 H), 4.81–6.10 (m, 3 H), 7.21 (s, 5 H); IR (liquid film, cm^{-1}) 2800–3100 (m), 1640 (m), 1450 (m), 1110 (s), 915 (m); MS, m/e (relative intensity) 121 (M^+ − 41, 100) 91 (15), 77 (25), 51 (9), 41 (3). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.63; H, 8.75.

4-Methoxy-1-nonene (7b): TLC (PhH/Hex, 1/1) R_f 0.85; NMR (CCl_4) δ 0.8–1.0 (m, 3 H), 1.1–1.6 (m, 8 H), 2.20 (t, J = 6 Hz, 2 H), 2.9–3.2 (m, 1 H), 3.30 (s, 3 H), 4.7–5.2 (m, 2 H), 5.4–6.1 (m, 1 H); IR (liquid film, cm^{-1}) 2940 (s), 1640 (m), 1460 (w), 1100 (m); MS, m/e (relative intensity) 115 (M^+ − 41, 96), 85 (35), 83 (100), 55 (93); high-resolution MS, $C_7H_{15}O$ (M^+ − 41) obsd m/e 115.1117 (calcd 115.1122).

4-Methoxy-5-methyl-1-octene (7c): TLC (PhH/Hex, 1/4) R_f 0.8; NMR (CCl_4) δ 0.8–1.1 (m, 6 H), 1.2–1.9 (m, 5 H), 2.3 (t, J = 6 Hz, 2 H), 2.9–3.1 (m, 1 H), 3.30 (s, 3 H), 4.9–5.2 (m, 2 H), 5.7–6.1 (m, 1 H); IR (liquid film, cm^{-1}) 2960 (s), 1640 (m), 1460 (m), 1380 (w), 1260 (w), 1100 (s), 920 (m), 860 (m); MS, m/e (relative intensity) 115 (M^+ − 41, 100), 85 (71), 83 (73), 56 (30), 50 (50), 41 (39); high-resolution MS, $C_7H_{15}O$ (M^+ − 41) obsd m/e 115.1124 (calcd 115.1123).

1-Methoxy-1-(2-propenyl)cyclohexane (7d): TLC (PhH/Hex, 1/1) R_f 0.8; NMR (CCl_4) δ 1.2–1.9 (m, 10 H), 2.15 (d, J = 7 Hz, 2 H), 3,15 (s, 3 H), 4.9–5.2 (m, 2 H), 5.6–6.1 (m, 1 H); IR (liquid film, cm^{-1}) 2940 (s), 1640 (w), 1480 (w), 1260 (m), 1090 (s), 860 (s); MS, m/e (relative intensity) 113 (M^+ − 41, 100), 81 (86), 71 (12); high-resolution MS, $C_7H_{13}O$ (M^+ − 41) obsd m/e 113.0970 (calcd 113.0967).

Reaction of Benzaldehyde (2a), Allylsilane (6), and Methanol Catalyzed by Iodine. Synthesis of 7a. Iodine (6 mg, 0.02 mmol) was added to a mixture of benzaldehyde (53 mg, 0.50 mmol), allyltrimethylsilane (229 mg, 2.0 mmol) and methanol (39 mg, 1.2 mmol) in dichloromethane (0.5 ml) and the resulting mixture was stirred at 40 °C for 1 h. The product **7a** (72 mg, 89% yield) was purified by TLC (silica gel) by using PhH/Hex (1/1) as an eluent.

Acknowledgment. The work was supported by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project No. 57118002). We also thank Toshiba Silicone Co., Ltd., and Mitsubishi Chemicals Co., Ltd., for gifts of chlorosilanes and tetramethoxysilane, respectively.

Registry No. **1**, 16029-98-4; **2a**, 100-52-7; **2b**, 108-94-1; **3a**, 681-84-5; **3b**, 7381-30-8; **4a**, 1125-88-8; **4b**, 10032-05-0; **4c**, 177-10-6; **6**, 18191-59-8; **7a**, 22039-97-0; **7b**, 90246-13-2; **7c**, 90246-14-3; **7d**, 60753-94-8; $CH_3(CH_2)_5CHO$, 29381-66-6; $CH_3(CH_2)_4CHO$, 66-25-1; $CH_3(CH_2)_2CH(CH_3)CHO$, 123-15-9; I_2, 7553-56-2.

(11) Mastagli, P.; Lambert, P.; Baladie, D. *C. R. Hebd. Seances Acad. Sci.* **1962**, *255*, 2978.
(12) Shono, T.; Nishiguchi, I.; Oda, R. *J. Org. Chem.* **1970**, *35*, 42.

An Unusual Oxidative Dimerization of 2-(Vinyloxy)phenols

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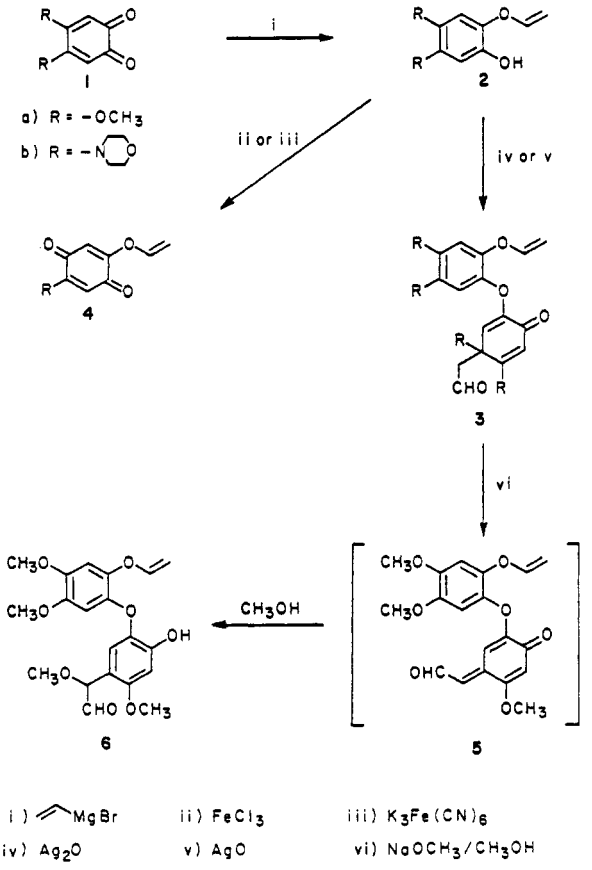
Received December 13, 1983

Reported here is an unusual oxidative dimerization of 2-(vinyloxy)phenols. Specifically, the phenols **2a** and **2b** were observed to give the respective dimers **3a** and **3b** in nearly quantitative yields when treated with either Ag_2O or AgO under anhydrous conditions at ambient temperature (Scheme I). A particularly interesting feature of this facile transformation is the observation that the vinyloxy group in one of the monomeric units has undergone a migration and conversion to an ethanal moiety, and this all takes place under the mild reaction conditions employed.

In attempts to isolate an intermediate in the transformations of **2a** and **2b** to their respective dimers, **3a** and **3b**, the Ag_2O oxidation of **2a** was carried out at low tem-

0022-3263/84/1949-2809$01.50/0

Scheme I



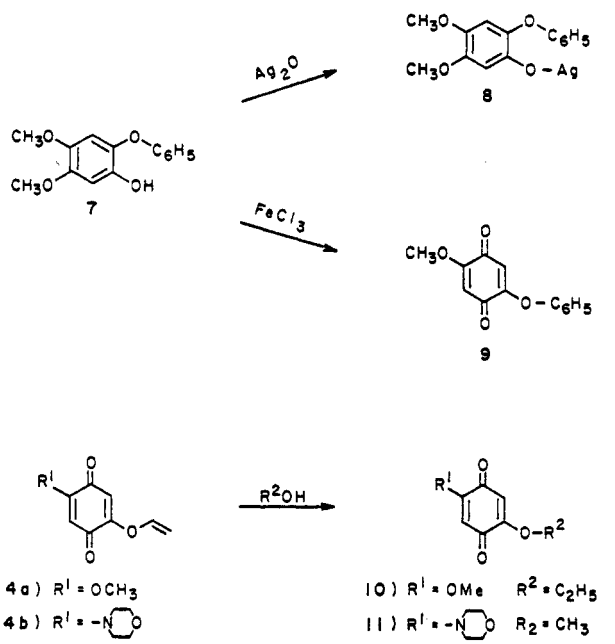
perature. No observable reaction took place until 0 °C and at this temperature the only produce was the dimer **3a**. Also, the utilization of other oxidizing agents did not provide an intermediate to **3a**. This study did, however, result in useful data since high yields (>90%) of the quinones **4a** and **4b** were realized when the corresponding (vinyloxy)phenols were treated with either $FeCl_3$ or $K_3Fe(CN)_6$. These transformations are worthy of note since they provide an efficient route to (vinyloxy)-1,4-benzoquinones, a rare, if not previously unknown, class of compounds which could conceivably be employed as precursors to a variety of other quinone derivatives. As an illustration, the vinyloxy group of **4a** was observed to be selectively replaced to give a 94% yield of 2-ethoxy-5-methoxy-1,4-benzoquinone (**10**) when an ethanolic solution was refluxed (Scheme II). Similarly, **4b** was converted to the methoxy analogue 11 (92%) in refluxing methanol.

Attempts to oxidize 2-phenoxy-4,5-dimethoxyphenol (**7**), by using the silver oxide conditions described above did not result in dimerization but, rather, gave the silver salt **8**. However, oxidation of **7** with $FeCl_3$ gave the expected phenoxyquinone **9** in excellent yield (91%).

The assigned structures of **3a**, **3b**, **4a**, and **4b** are in complete accord with their observed spectral data (Experimental Section). In addition, chemical evidence was obtained which further substantiates the structure of **3a**. Specifically, it was converted to the phenol **6** in 94% yield upon treatment with sodium methoxide in methanol, a reaction which most likely involves the quinone methide **5**.

Possible mechanistic pathways for the conversion of phenols **2a** and **2b** to the dimers **3a** and **3b** are outlined in Scheme III. The free radical *13* is a reasonable intermediate and is envisaged as arising from attack of **12** on a molecule of starting phenol **2**. Oxidative conversion of **13** to **15** is also a reasonable process. However, the

Scheme II



proposed [3,3]-sigmatropic rearrangement of **15** to **16** would be unusual in view of the mild reaction conditions employed for these oxidative dimerizations. An intriguing alternate mechanistic interpretation is that the sigmatropic rearrangement takes place directly from the radical **13** to give the radical **14**. Subsequent oxidation of **14** would then give the dimer **16**. The partial structure **17** represents that fragment undergoing the sigmatropic rearrangement; such a structure may allow the rearrangement to be assisted by the radical center. This would be in analogy to the well-known alkoxide-assisted Cope rearrangements (structure **18**) initially described by Evans and Golob[1] as well as the more recently reported carbanion analogies of the Claisen rearrangement (structure **19**) described by Denmark and Harmata.[2] To our knowledge, no data exists on radical-assisted [3,3]-sigmatropic rearrangements.

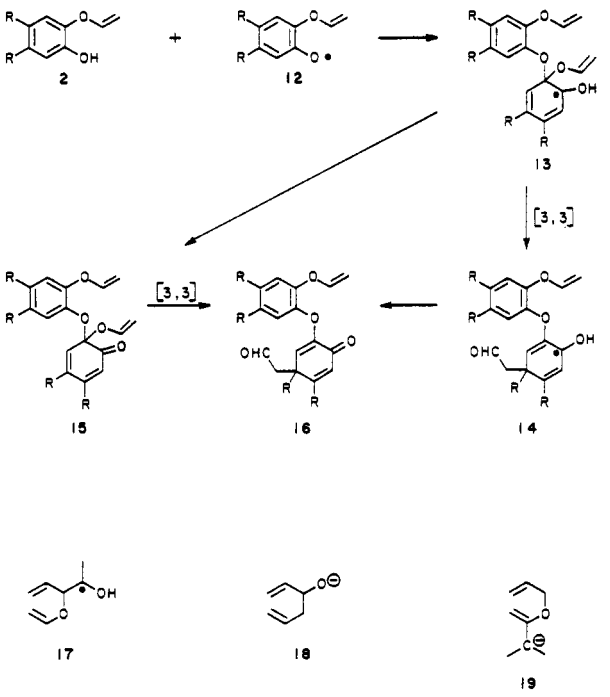
Finally, it should be noted that the results presented here provide a potentially general route to dienones of structural type **16** as well as the unsymmetrically substituted quinones **4a**, **4b**, and **9**. Furthermore, the starting (vinyloxy)phenols **2a** and **2b** were readily obtained in yield greater than 80% when 4,5-dimethoxy-1,2-benzoquinone (**1a**) and 4,5-dimorpholino-1,2-benzoquinone (**1b**) were treated with the appropriate vinyl or aryl magnesium bromides.[3,4]

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus or a Fisher-Jones apparatus and are uncorrected. Microanalyses were performed by Robertson's Laboratory, Florham Park, NJ. ^1H NMR spectra were obtained on Varian FT-80 and Bruker WM-250 spectrometers. All chemical shifts are reported relative to the internal standard tetramethylsilane (Me_4Si) as values in parts per million. The spectra were obtained on $CDCl_3$ solutions (1% Me_4Si, v/v) unless otherwise specified. Coupling constants (J) are apparent unless otherwise stated, and the multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared spectra were determined with a Perkin-Elmer 137 sodium chloride spectrometer on CH_2Cl_2 solutions unless otherwise specified. The

(1) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.
(2) Denmark, S. E.; Harmata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4972.
(3) Wage, D. *Aust. J. Chem.* **1971**, *24*, 1531.
(4) Ito, Y.; Kakuta, K.; Hirano, M.; Morimoto, J. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2169.

Scheme III



positions of the absorption bands are express in cm^{-1} and polystyrene was used as an reference. Mass spectra were determined on a medium-resolution Finnigan 4000 GC/MS quadrupole spectrometer which was interfaced to a Nova 312 data system. High-resolution mass spectra were obtained from Midwest Center for Mass Spectrometry, Lincoln, NE 68588.

Analytical reagent-grade solvents were used in all experiments unless otherwise specified. Tetrahydrofuran is abbreviated as THF and was freshly distilled from potassium. All reactions (unless otherwise specified) were run in flame-dried glassware filled with argon which had been dried by passage through a column of Drierite.

Solvents were removed by concentration on a Roto-vap under reduced pressure. The silica gel used in column chromatography was EM-60 supplied by Merck and was 70–230 mesh size.

4,5-Dimethoxy-2-(vinyloxy)phenol (2a). To a solution of 1.00 g (5.95 mmol) of 4,5-dimethoxy-1,2-benzoquinone[4] (**1a**) in 500 mL of THF at −78 °C was added dropwise via syringe 18 mL (18 mmol) of vinylmagnesium bromide (1.0 m in THF). The solution was stirred at −78 °C for 30 min and then allowed to warm to room temperature. The reaction mixture was quenched with aqueous ammonium chloride, the organic layer were removed, and the aqueous layer was washed with 100 mL of dichloromethane. The organic layers were combined and dried and the product isolated via flash chromatography (1:1 hexane/ethyl acetate) to give 1.01 g (87%) of a white solid which was recrystallized from petroleum ether: mp 59–60 °C; NMR 6.56 (d of d, J = 13.8 Hz, J = 6.2 Hz, 1 H), 6.59 (s, 2 H), 5.43 (br, 1 H), 4.60 (d of d, J = 13.8 Hz, J = 2.1 Hz, 1 H) 4.37 (d of d, J = 6.2 Hz, J = 2.1 Hz, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H); IR 3357, 3441, 2943, 2840, 1662, 1503; MS 196 (EI), 197 (CI).

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.20; H, 6.16. Found: C, 61.20; H, 6.37.

4,5-Dimethoxy-2-phenoxyphenol (7). To a solution of 1.00 g (5.95 mmol) of 4,5-dimethoxy-1,2-benzoquinone[4] (**1a**) in 500 mL of THF at −78 °C was added dropwise, via syringe, 5.80 mL (18 mmol) of phenylmagnesium bromide (3.1 m in THF). The solution was stirred at −78 °C for 30 min and then allowed to warm to room temperature. The reaction mixture was quenched with aqueous ammonium chloride, the organic layer removed, and the aqueous layer washed with 100 mL of dichloromethane. The organic layers were combined and dried and the product isolated via flash chromatography (1:1 hexane/ethyl acetate) to give 1.27 g (81%) of an oil which was crystallized from diisopropyl ether: mp 74–75 °C; NMR 7.08 (m, 5 H), 6.63 (s, 1 H), 6.54 (s, 1 H), 3.81 (s, 3 H), 3.69 (s, 3 H); IR, 3559, 3452, 2944, 2839, 1594, 1491; MS, 246 (EI), 247 (CI).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.20; H, 5.46.

4,5-Dimorpholino-2-(vinyloxy)phenol (2b). To a solution of 1.00 g (3.59 mmol) of 4,5-dimorpholino-1,2-benzoquinone[5] (**1b**) in 500 mL of THF at −78 °C was added dropwise, via syringe, 11 mL (11 mmol) of vinylmagnesium bromide (1.0 m in THF). The solution was stirred at −78 °C for 30 min and then allowed to warm to ambient temperature. The reaction mixture was quenched with aqueous ammonium chloride, the organic layer removed, and the aqueous layer washed with 100 mL of dichloromethane. The organic layers were combined and dried, and the product was isolated via flash chromatography (1:1 hexane/ethyl acetate) to give 778 mg (71%) of an oil which was crystallized from methanol: mp 157.5–158.5 °C; NMR 6.58 (s, 2 H), 6.56 (d of d, J = 13.7 Hz, J = 6.2 Hz, 1 H), 5.21 (br, 1 H), 4.67 (d of d, J = 13.7 Hz, J = 2.1 Hz, 1 H), 4.41 (d of d, J = 6.2 Hz, J = 2.1 Hz, 1 H), 3.81 (m, 8 H), 3.17 (m, 8 H); IR, 3562, 3318, 2957, 1641, 1598, 1501.

Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.73; H, 7.24. Found: C, 62.66; H, 7.36.

3,4-Dimethoxy-4-(2-oxoethyl)-6-[4,5-dimethoxy-6-(vinyloxy)phenoxy]-2,5-cyclohexadienone (3a). A solution of 500 mg (2.55 mmol) of 4,5-dimethoxy-2-(vinyloxy)phenol (**2a**) in 50 mL of dry ether was stirred under argon with Ag_2O and hydrous magnesium sulfate. TLC analysis showed the reaction to be complete in 15 min. The mixture was filtered through Celite. Removal of the solvent gave 965 mg (97%) of an oil which was >95% pure by NMR and HPLC analysis of the crude reaction product: NMR 9.67 (t, J = 2.6 Hz, 1 H), 6.70 (s, 1 H), 6.68 (s, 1 H), 6.47 (d of d, J = 13.7 Hz, J = 6.2 Hz, 1 H), 5.79 (s, 1 H), 5.29 (s, 1 H), 4.52 (d of d, J = 13.7 Hz, J = 2.0 Hz, 1 H), 4.30 (d of d, J = 6.2 Hz, J = 2.0 Hz, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.14 (s, 3 H), 2.73 (t, J = 3.0 Hz, 2 H); IR 2948, 1732, 1680, 1651, 1622, 1522; MS, 390 (EI), 391 (CI); exact mass calcd for $C_{20}H_{22}O_8$ 390.1314, found 390.1302.

Dimer **3a** was also prepared by a procedure which was identical with the above using AgO. The reaction was complete in 5 min and gave **3a** in 96% yield.

3,4-Dimorpholino-4-(2-oxoethyl)-6-[4,5-dimorpholino-2-(vinyloxy)phenoxy]-2,5-cyclohexadienone (3b). A solution of 500 mg (2.55 mmol of 4,5-dimorpholino-2-(vinyloxy)phenol (**2b**) in 50 mL of dry ether was stirred under argon with AgO and anhydrous magnesium sulfate. TLC analysis of the reaction solution showed the reaction to be complete in 3 h. The mixture was filtered through Celite and the Celite washed with ether. Removal of the solvent gave 965 mg (97%) of an oil which decomposed within hours at room temperature. However, it was stable for several months at 0 °C in an ethereal solution: NMR 9.67 (t, J = 2.6 Hz, 1 H), 6.70 (s, 1 H), 6.68 (s, 1 H), 6.49 (d, of d, J = 13.7 Hz, J = 6.2 Hz, 1 H), 5.79 (s, 1 H), 5.29 (s, 1 H), 4.52 (d of d, J = 13.7 Hz, J = 2.0 Hz, 1 H), 4.30 (d of d, J = 6.2 Hz, J = 2.0 Hz, 1 H), 3.82 (m, 8 H), 3.31 (m, 8 H), 2.73 (t, J = 3.0 Hz, 2 H); IR 2979, 1664, 1624, 1572; exact mass calcd for $C_{32}H_{42}N_4O_8$ 610.3002, found 610.3014.

4-(2-Oxo-1-methoxyethyl)-3-methoxy-2-[3,4-dimethoxy-6-(vinyloxy)phenoxy]phenol (6). A solution of 100 mg of 3,4-dimethoxy-4-(2-oxoethyl)-6-[4,5-dimethoxy-6-(vinyloxy)-phenoxy]-2,5-cyclohexadienone (**3a**) in 50 mL of anhydrous methanol was stirred under argon while 50 mg of solid sodium methoxide was added. TLC analysis of the reaction mixture indicated the reaction to be complete immediately upon addition of the base. Ether was added and the mixture washed with 1 N HCl. The organic layer was collected and dried and the product isolated via preparative TLC to give 94 mg (94%) of an oil which was determined to be >95% pure by NMR and HPLC analysis. NMR 9.51 (d, J = 0.8 Hz, 1 H), 6.79 (s, 1 H), 6.66 (s, 1 H), 6.63 (s, 2 H), 6.51 (d, of d, J = 13.8 Hz, J = 6.2 Hz, 1 H), 6.09 (br, 1 H), 4.92 (s, 1 H), 4.43 (d of d, J = 13.8 Hz, J = 2.1 Hz, 1 H), 4.29 (d of d, J = 6.2 Hz, J = 2.1 Hz, 1 H), 3.86 (s, 3 H), 3.80 (s, 3 H), 3.78 (s, 3 H) 3.34 (s, 3 H); IR 3542, 1737, 1505, 1203, 1103; exact mass calcd for $C_{20}H_{22}O_8$ 390.1314, found 390.1306.

3-Methoxy-6-(vinyloxy)-1,4-benzoquinone (4a). 4,5-Dimethoxy-2-(vinyloxy)phenol (**2a**) (100 mg, 0.510 mmol) was

(5) Brackman, W.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1975**, *74*, 937.

dissolved in 50 mL of ether and stirred with 10 mL of saturated aqueous ferric chloride. TLC analysis showed the reaction to be complete within 10 min. The organic layer was removed, washed well with water, and dried. Removal of the solvent gave 85.5 mg (93%) of a yellow solid which was recrystallized from diisopropyl ether: mp 166.5–167.5 °C; NMR 6.50 (d of d, J = 13.0 Hz, J = 5.9 Hz), 6.01 (s, 1 H), 5.91 (s, 1 H), 5.21 (d of d, J = 13.0 Hz, J = 2.3 Hz, 1 H), 4.90 (d of d, J = 5.9 Hz, J = 2.3 Hz, 1 H), 3.86 (s, 3 H); IR 1673, 1601, 1195.

Anal. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 60.30; H, 4.68.

2-Methoxy-5-phenoxy-1,4-benzoquinone (9). By a procedure analogous to that described above, 100 mg (0.406 mmol) of 4,5-dimethoxy-2-phenoxyphenol (**7**) gave 85 mg (91%) of a yellow solid which was recrystallized from diisopropyl ether: mp 139.5–140.5 °C; NMR 7.0–7.5 (m, 5 H), 5.95 (s, 1 H), 5.64 (s, 1 H), 3.86 (s, 3 H); IR 3070, 1680, 1613, 1597, 1212, 1199, 1187.

Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.46; H, 4.51.

2-Morpholino-5-(vinyloxy)-1,4-benzoquinone (4b). By a procedure analogous to that described above 200 mg (0.652 mmol) of 4,5-dimorpholino-2-(vinyloxy)phenol (**2b**) was converted to 143 mg (93%) of **4b**: red-orange plates; mp 204–205 °C; NMR 6.49 (d of d, J = 13.0 Hz, J = 5.9 Hz, 1 H), 5.85 (s, 1 H) 5.65 (s, 1 H), 5.08 (d of d, J = 13.0 Hz, J = 2.3 Hz, 1 H), 4.78 (d of d, J = 5.9 Hz, J = 2.3 Hz, 1 H), 3.75 (s, 4 H), 3.50 (m, 4 H); IR 1665, 1624, 1578.

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57. Found: C, 61.22; H, 5.54.

2-Ethoxy-5-methoxy-1,4-benzoquinone (10). A solution of 100 mg (0.555 mmol) of 2-methoxy-5-(vinyloxy)-1,4-benzoquinone (**4a**) in 100 mL of absolute ethanol was refluxed for 6 h. The solvent was removed in vacuo to give a yellow solid which was recrystallized from diisopropyl ether to give 95 mg (94%) of **10**: mp 197–198 °C (lit.[6] mp 197.5–198.5 °C); NMR 5.86 (s, 1 H), 5.84 (s, 1 H), 4.04 (q, J = 7 Hz, 2 H), 3.84 (s, 3 H), 1.49 (t, J = 7 Hz, 3 H).

2-Methoxy-5-morpholino-1,4-benzoquinone (11). A solution of 100 mg (0.426 mmol) of 2-morpholino-5-(vinyloxy)-1,4-benzoquinone (**4b**) in 100 mL of absolute methanol was refluxed for 6 h. Removal of the solvent in vacuo gave an orange red solid which was recrystallized from methanol to give 87.5 mg (92%) of **11**: mp 190–192 °C; NMR 5.69 (s, 1 H), 5.62 (s, 1 H), 3.80 (m, 7 H), 3.14 (m, 4 H); IR, 1668, 1620, 1580.

Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.18: H, 5.85. Found: C, 59.14; H, 5.58.

Acknowledgment. We thank the National Institutes of Health (CA 11890) for financial support of this work.

Registry No. **1a**, 21086-65-7; **1b**, 4608-10-0; **2a**, 90433-59-3; **2b**, 90433-60-6; **3a**, 90433-61-7; **3b**, 90433-62-8; **4a**, 90433-63-9; **4b**, 90433-64-0; **6**, 90433-65-1; **7**, 90433-66-2; **8**, 90433-67-3; **9**, 90433-68-4; **10**, 75080-61-4; **11**, 90433-69-5; Ag_2O, 20667-12-3; AgO, 1301-96-8; $FeCl_3$, 7705-08-0; $K_3Fe(CN)_6$, 13746-66-2; vinyl bromide, 593-60-2; phenyl bromide, 108-86-1.

(6) Cole, E. R.; Crank, G.; Hai Minh, H. T. *Aust. J. Chem.* **1980**, *33*, 527.

Benzopyrans. 17.[1] Triethylamine-Mediated Transformation of 4-Oxo-4*H*-1-benzopyran-3-carboxaldehyde[2]

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Received December 2, 1983

So far as their reactions with a secondary aliphatic or aromatic amine are concerned, both the title aldehyde **1** and the corresponding acid **2** (Chart I) behave similarly to give the enamino ketone **9**.[3,4] The acid **2** on treatment

Scheme I

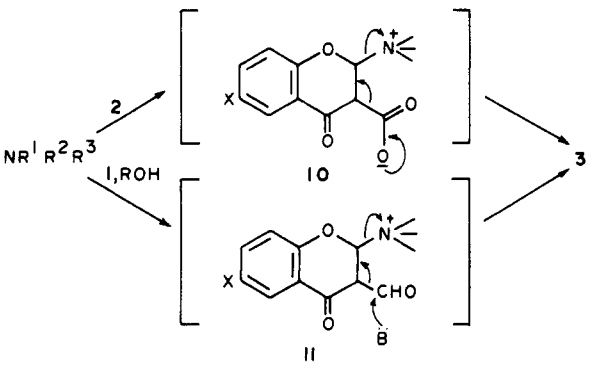

Table I. Triethylamine-Mediated Transformation Products of Chromone-3-carboxaldehyde (1)

X in 1/R of ROH	yield, % (mp, °C), of the products[a]			
	4	5	6	7
H/Me	*b*	10 (162)		7 (158)
Me/Et		8 (200)	6 (196)	
OMe/Me		15 (180)		
Cl/Me	30 (116)			
Br/Me	24 (108)		6 (210)	75 (280)[c]
Br/Et			56 (210)	80 (306)[c]
NO_2/Me	22 (142)			

[a] Only **3a** could be isolated in 2% yield by column chromatography, **3b,c** being detected by TLC; all the chromones **3** are known compounds (see ref 3 and references cited therein). Each of the products **8** obtained in 2–3% yield decomposed above 300 °C. [b] Detected by co-TLC with authentic sample. [c] Obtained by acid-catalyzed isomerization of **6** in the appropriate alcohol.

Table II. 3-(Dimethoxymethyl)-4-oxo-4*H*-1-benzopyrans 4 (R = Me)[a]

X	mp, °C	^{1}H NMR ($CDCl_3$), δ: H-5[b]	H-2[c]	other Ar H[b]	CH-$(OR)_2$[c]	$(OR)_2$
H	80	8.25	8.10	7.80–7.28	5.58	3.42 (s)
Cl	116	8.18	8.08	7.76–7.24	5.56	3.40 (s)
Br	108	8.32	8.08	7.84–7.28	5.56	3.40 (s)
NO_2	142	9.10	8.20	8.35–7.78	5.60	3.44 (s)

[a] Satisfactory analytical data (±0.4%) for C and H were obtained. [b] Aromatic protons show normal splitting. [c] Doublet due to allylic coupling, J = 0.8 Hz.

Table III. ^{1}H NMR, δ, for 2,3-Dihydro-2-(4-oxo-4*H*-1-benzopyran-3-yl)-4-oxo-4*H*-1-benzopyrans 5[a]

	vinyl H	Ar H (m)	Hx (m)	$H_A + H_B$[b]	X (s)
5a	8.72–7.00		5.72	3.00	
5b[c]	8.20[d]	8.04–6.92	5.72	3.00	2.46, 2.32
5c	8.24[d]	7.56–6.88	5.68	3.00	3.86, 3.78

[a] All the compounds gave satisfactory elemental analyses: C, ±0.36; H, ±0.37. [b] These two protons appear as dq, J_{AB} = 16 Hz, J_{AX} = 3 Hz, and J_{BX} = 14 Hz. [c] UV (EtOH) λ 220 (log ε 4.46) and 305 (4.07) nm; IR ($CHCl_3$) ν 1685 (4′-CO), 1635 (4-CO), 1610 (C=C) cm^{-1}; mass spectrum, m/e 320 (M^+), 303 (M – OH), 291 (M – H – CO), 275 (M – OH – CO), 213, 184. [d] Doublet due to allylic coupling, J = 0.8 Hz.

(1) Part 16: Ghosh, C. K.; Tewari, N.; Bhattacharyya, A. *Indian J. Chem.*, in press.
(2) For a preliminary account, see: Ghosh, C. K.; Bandyopadhya, C.; Tewari, N. "Proceedings of the Ninth International Congress of Heterocyclic Chemistry"; Tokyo, Aug 21–26, 1983; Abstr. No. G-100.
(3) Ghosh, C. K.; Khan, S. *Synthesis* **1981**, 719.

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