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Notes

Protection of a Substituted Catechol Whose Derivatives Are Subject to Steric Labilization

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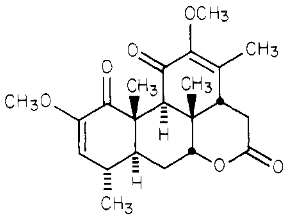
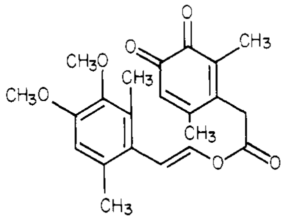
In the course of an effort directed toward the synthesis of quassin, 1, it was of interest to prepare the styryl *o*-quinone 2, to study the possibility of effecting an intramolecular Diels–Alder reaction. Toward this end we planned to use an approach developed earlier in the synthesis of 3.[2] In this instance we wished to synthesize 4, which should be converted to 2 by oxidation with Ag_2O.[3] For this reason we synthesized 5 as shown in Scheme I.



1



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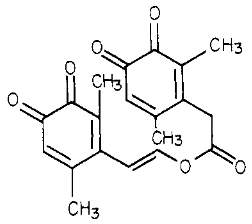

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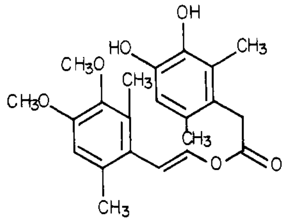

4

We had thought that with trimethylsilyl iodide the cleavage of the benzyl ethers in 5 would be much more rapid than the methyl ethers[4] and thus from 5 we should be able to generate 4. In fact, this was not the case and monitoring the reaction by NMR spectroscopy revealed the order of cleavage was first the C(12) benzyl ether, followed by the C(1) methyl ether and finally the C(11) benzyl ether.[5] This type of "steric labilization" of a hindered methoxyl is precedented[6] although the preferred cleavage of a methyl ether relative to a benzyl ether is unexpected.

To circumvent this difficulty we prepared 16 following the chemistry we had developed earlier (Scheme II). Our anticipation was that the lowered reactivity of ethyl ethers as compared to methyl ethers toward cleavage with trimethylsilyl iodide[4] would provide us with the desired selectivity. However, most surprisingly, even with compound 16 selective cleavage of the benzyl ethers could not be realized.

The problem was finally solved with the synthesis of 20, given in Scheme III. It was found that 20 could be smoothly cleaved to 21 without the attending difficulties experienced with 5 and 16. We feel the stability of the 1,2-ethylenedioxy grouping toward trimethylsilyl iodide cleavage reflects the difficulty of obtaining an S_N2 displacement at a carbon with a β-alkoxy substituent.[7]

Subsequently, 21 was oxidized to 22 with Ag_2O. Attempts at realizing intramolecular Diels–Alder cyclization of 22 have not been successful.

Experimental Section

Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were taken on a Varian EM 390 (90 MHz) or a Varian EM 360 (60 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane, which was used as the internal standard. Coupling constants (J) are reported in hertz (Hz). Infrared spectra were taken on a PE 257, a PE 467, or a PE 727B spectrometer and are reported in reciprocal centimeters (cm^{-1}). Polystyrene film was used to calibrate spectra at 1601 cm^{-1}. Mass spectra were taken on a Finnigan 4000 GC/MS. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

(Dihydroxyphenyl)acetic Ester 7. A flask containing 4.0 g (16.8 mmol) of 6[2] in 20 mL of dry methylene chloride was purged with nitrogen and cooled to −78 °C. Boron tribromide (8.0 mL, 84.6 mmol) was added all at once and the reaction mixture allowed to warm to room temperature and stirred for 35 min. After the mixture was again cooled to −78 °C, 5 mL of water was carefully added and the reaction mixture allowed to warm to room temperature. The solution was diluted with methylene chloride and washed with water which was back-extracted with methylene chloride. The combined extracts were washed with brine and dried over sodium sulfate. Removal of the solvent in vacuo afforded 3.7 g (98%) of 7 as a colorless solid: mp 110.0–111.0 °C; NMR (60 MHz, $(CD_3)CO$) δ 1.23 (t, 3 H, J = 7 Hz), 2.23 (s, 6 H), 2.59 (s, 2 H), 4.09 (q, 2 H, J = 7 Hz), 6.08 (s, 1 H); IR (KBr) 3490, 3250, 2950, 1710, 1610, 1510, 1475, 1370, 1340, 1290, 1200, 1110, 1020, 980, 920, 845 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.29; H, 7.20.

[Bis(benzyloxy)phenyl]acetic Ester 8. Catechol 7 (4.01 g, 17.9 mmol) and 25.0 g (179 mmol) of potassium carbonate in 100 mL of acetone saturated with potassium carbonate were stirred at reflux under an atmosphere of nitrogen for 30 min. Benzyl bromide (8.52 mL, 71.6 mmol) was added all at once and the reaction mixture was stirred at reflux for an additional 36 h. The solvent was removed in vacuo, and the residue was diluted with water and extracted 3 times with ether. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure and removal of the excess benzyl bromide under a high vacuum provided 7.26 g of crude benzyl ether. Chromatography on silica gel with ether/hexanes as the eluent gave 7.06 (97%) of 8 as a colorless solid:

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(1) This work is abstracted in part from the Ph.D. theses of D. E. L. and L. F. C., Emory University, Atlanta, GA, 1981.

(2) Mandell, L.; Lee, D. E.; Courtney, L. F. *J. Org. Chem.* **1982**, *47*, 610.

(3) Grundmann, C. *Methoden Org. Chem. (Houben-Weyl)* **1979**, *VII/3b*, 42–44.

(4) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. McOmie, J. F. W., "Protective Groups in Organic Chemistry"; Plenum Press: New York, 1976; p 157.

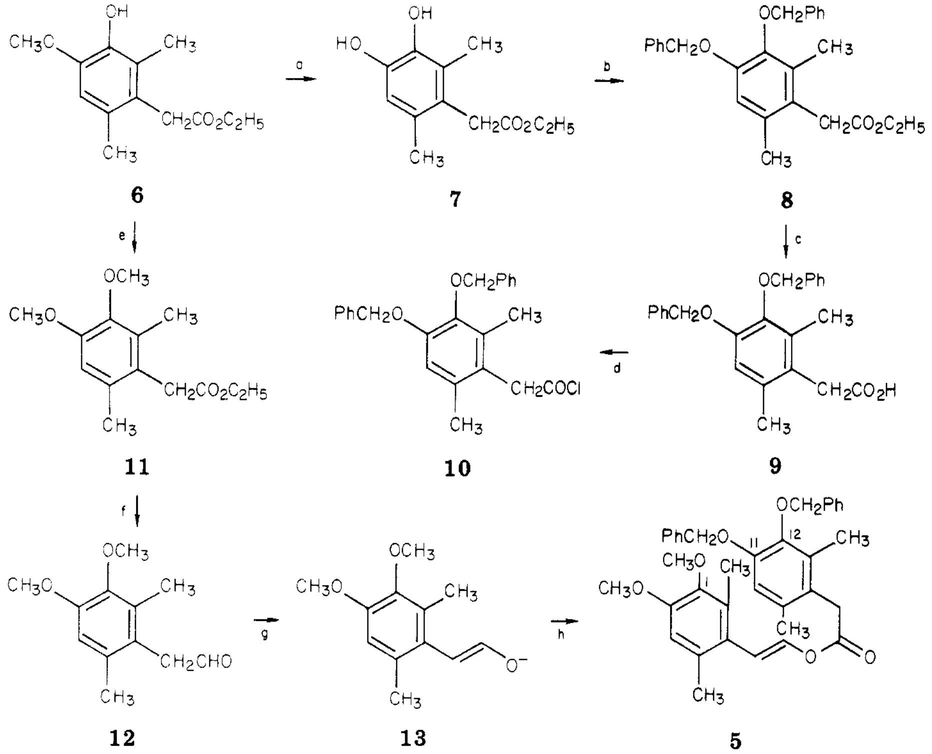
(5) The numbering given for 5 follows that in quassin for the sake of simplicity.

(6) Vickery, E. H.; Pahler, L. F.; Eisenbraun, E. J. *J. Org. Chem.* **1979**, *44*, 4444. Minamikawa, J.; Brossi, A. *Tetrahedron Lett.* **1978**, 3085. Minamikawa, J.; Brossi, A. *Can. J. Chem.* **1979**, *57*, 1720. Teitel, S., Brossi, A. *Heterocycles* **1973**, *1*, 73.

(7) Klemperer, W.; MCabe, L.: Sindler, B. *J. Am. Chem. Soc.* **1952**, *74*, 3425. Streitweiser, A. *Chem. Rev.* **1956**, *56*, 685.

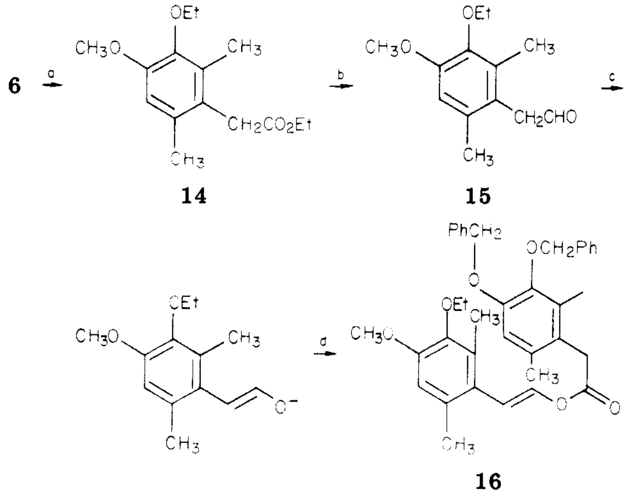
0022-3263/82/1947-0731$01.25/0

Scheme I[a]



[a] (a) BBr_3, (b) K_2CO_3, $PhCH_2Br$, (c) NaOH, (d) $(COCl)_2$, (e) CH_3I, K_2CO_3, (f) DIBAL-H, (g) lithium 2,2,6,6-tetramethylpiperidide, (h) compound **10**.

Scheme II[a]

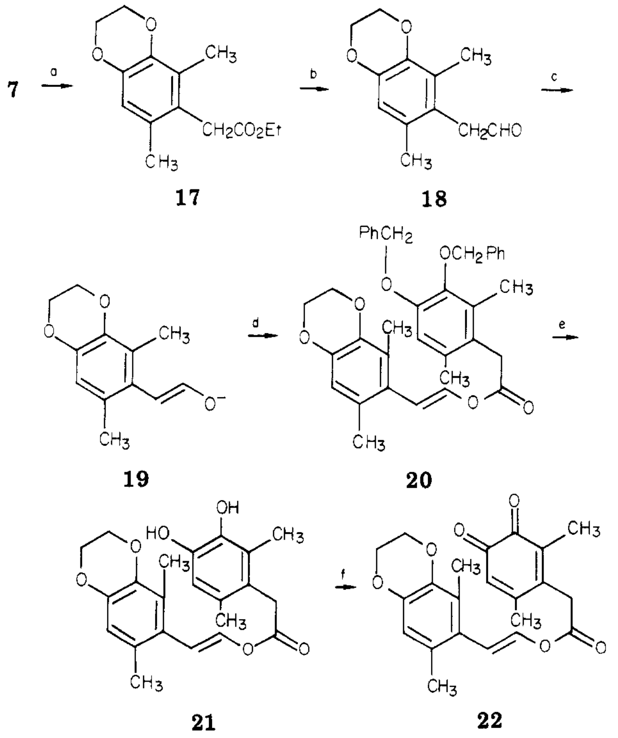


[a] (a) K_2CO_3, CH_3CH_2I, (b) DIBAL-H, (c) lithium 2,2,6,6-2,2,6,6-tetramethylpiperidide, (d) compound **10**.

mp 50.0–51.0 °C; NMR (90 MHz, $CDCl_3$) δ 1.22 (t, 3 H, J = 7 Hz), 2.27 (s, 3 H), 2.31 (s, 3 H) 3.63 (s, 2 H), 4.15 (q, 2 H, J = 7 Hz), 4.98 (s, 2 H), 5.10 (s, 2 H), 6.74 (s, 1 H), 7.34 (m, 10 H); IR ($CHCl_3$) 3040, 1725, 1600, 1490, 1460, 1375, 1330, 1285, 1220, 1160, 1110, 1035, 920, 850 cm^{-1}. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.27; H, 7.00.

[Bis(benzyloxy)phenyl]acetic Acid 9. Compound **8** (6.63 g, 16.4 mmol) and 3.28 g (82.0 mmol) of sodium hydroxide in 100 mL of a 50/50 mixture of methanol/water were stirred at room temperature for 12 h. The solvent was removed in vacuo, diluted with water, and washed with two portions of methylene chloride. The alkaline aqueous phase was made acidic with dilute hydrochloric acid and extracted 3 times with methylene chloride. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave 5.99 g (97%) of **9** as a colorless solid: mp 140–141.0 °C; NMR (60 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 2.33 (s, 3 H), 3.67 (s, 2 H), 4.98 (s, 2 H), 5.10 (s, 2 H), 6.79 (s, 1 H), 7.48 (m, 10 H); IR ($CHCl_3$) 3050, 2975, 2910, 1718, 1600, 1460, 1420, 1385, 1340, 1285, 1230, 1120, 1080, 1000 cm^{-1}. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.56; H, 6.45. Found: C, 76.52; H, 6.45.

Scheme III[a]



[a] (a) K_2CO_3, $BrCH_2CH_2Br$, (b) DIBAL-H, (c) lithium 2,2,6,6-tetramethylpiperidide, (d) compound **10**, (e) TMSI, (f) Ag_2O.

[Bis(benzyloxy)phenyl]acetyl Chloride 10. Compound **9** (4.00 g, 10.6 mmol) was dissolved in 50 mL of dry benzene and the flask was purged with nitrogen. Oxalyl chloride (1.11 mL, 12.7 mmol) was added all at once and the mixture stirred at room temperature for 14 h. The solvent, excess oxalyl chloride, and byproducts were removed in vacuo to provide 4.19 g (100%) of **10** as a slightly yellow solid. The acid chloride is not purified further but used immediately to prepare enol ester **5**. **10**: NMR (60 MHz, $CDCl_3$) δ 2.19 (s, 3 H), 2.28 (s, 3 H), 4.11 (s, 2 H), 4.93 (s, 2 H), 5.09 (s, 2 H), 6.73 (s, 1 H), 7.39 (m, 10 H).

Dimethoxy Bis(benzyloxy) Enol Ester 5. Lithium 2,2,6,6-tetramethylpiperidide was prepared as follows. To a dry flask containing a trace of 2,2′-bipyridyl as an indicator was added 5 mL of dry tetrahydrofuran. The flask was purged with argon and cooled to 0 °C. 2,2,6,6-Tetramethylpiperidine (1.48 mL, 8.77 mmol) was added followed by the dropwise addition of 5.48 mL (8.77 mmol) of 1.6 M *n*-butyllithium in hexanes. The reaction mixture was warmed to room temperature and stirred for 15 min to afford 8.77 mmol of lithium 2,2,6,6-tetramethylpiperidide.

To a cooled solution (o °C) of lithium 2,2,6,6-tetramethylpiperdide in THF was added 1.66 g (7.97 mmol) of **12** in THF dropwise. After the addition was complete the reaction mixture was warmed to room temperature and stirred for 45 min still under an atmosphere of argon. Compound **10** (4.19 g, 10.6 mmol) was then added to the flask all at once and the reaction mixture was stirred at reflux for 3 h. The solvent was removed in vacuo and the residue diluted with ethyl acetate. This solution was washed with 10% hydrochloric acid and water, and the aqueous phases were back-extracted with ethyl acetate. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure provided 3.70 g of crude enol ester. The crude oil was chromatographed on silica gel with ether/hexanes as the eluent to afford 1.49 g (33%) of **5** as a colorless solid: NMR (90 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 2.34 (s, 6 H), 2.36 (s, 3 H), 3.83 (s, 2 H), 3.89 (s, 3 H), 3.92 (s, 3 H), 5.14 (s, 2 H), 5.25 (s, 2 H), 6.48 (d, 1 H, J = 13.5 Hz), 6.82 (s, 1 H), 6.98 (s, 1 H), 7.62 (m, 11 H); IR ($CHCl_3$) 3050, 2975, 1750, 1670, 1600, 1495, 1475, 1465, 1385, 1333, 1280, 1230, 1155, 1130, 1078, 1040 cm^{-1}. Anal. Calcd for $C_{36}H_{38}O_6$: C, 76.29; H, 6.77. Found: C, 76.27; H, 6.79.

(Dimethoxyphenyl)acetic Ester 11. Compound **6** (7.37 g, 30.9 mmol) and 21.37 g (155 mmol) of potassium carbonate in 100 mL of acetone saturated with potassium carbonate were stirred at reflux under a nitrogen atmosphere for 30 min Methyl iodide (3.85 mL, 61.8 mmol) was added all at once and the reaction mixture was stirred at reflux for an additional 14 h. The solvent was removed in vacuo, and the residue diluted with water and extracted 3 times with ether. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure provided 7.33 g of crude **11**. Chromatography on silica gel with ether/hexanes as the eluent gave 6.86 g (88%) of **11** as a colorless solid: NMR (60 MHz, $CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz), 2.28 (s, 3 H), 2.33 (s, 3 H), 3.62 (s, 2 H), 3.68 (s, 3 H), 3.78 (s, 3 H), 4.14 (q, 2 H, J = 7.0 Hz), 6.62 (s, 1 H); IR ($CHCl_3$) 3040, 2980, 1730, 1610, 1500, 1475, 1385, 1340, 1240, 1170, 1120, 1095, 1040, 1010, 860 cm^{-1}.

(Dimethoxyphenyl)acetaldehyde 12. Compound **11** (6.78 g, 26.9 mmol) was dissolved in 50 mL of dry ether and the flask was purged with nitrogen and cooled to −78 °C. A 40.3-mL (40.3 mmol) sample of 1 M diisobutylaluminum hydride in hexanes was added to the solution dropwise, and the mixture was stirred at −78 °C for 30 min. The reaction was quenched with saturated ammonium chloride and the mixture allowed to warm slowly to room temperature. This was diluted with ether and washed with 10% hydrochloric acid, 10% sodium hydroxide, and water. Each aqueous wash was back-extracted with ether. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure provided 5.55 g of the crude aldehyde. Chromatography on silica gel with ether/hexanes as the eluent afforded 5.43 g (97%) of **12** as a colorless solid: mp 40.0–41.0 °C; NMR (90 MHz, $CDCl_3$) δ 2.13 (s, 3 H), 2.18 (s, 3 H), 3.62 (d, 2 H, J = 3.0 Hz), 3.74 (s, 3 H), 3.80 (s, 3 H), 6.71 (s, 1 H), 9.61 (t, 1 H, J = 3.0 Hz); IR ($CHCl_3$) 3050, 2970, 2880, 2760, 1720, 1605, 1495, 1475, 1140, 1295, 1245, 1120, 1020, 855 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.20; H, 7.77.

(Methoxyethoxyphenyl)acetic Ester 14. Compound **6** was treated as in the procedure used in the conversion of **6** to **11**, with potassium carbonate and ethyl iodide to give **14** as a colorless solid in 95% yield after chromatography on silica gel with ether/hexanes as the eluent: NMR (60 MHz, $CDCl_3$) δ 1.28 (t, 3 H, J = 7.0 Hz), 1.39 (t, 3 H, J = 7.0 Hz), 2.28 (s, 3 H), 2.35 (s, 3 H), 3.67 (s, 2 H), 3.86 (s, 3 H), 4.00 (q, 2 H, J = 7.0 Hz), 4.18 (q, 2 H, J = 7.0 Hz), 6.68 (s, 1 H).

(Methoxyethoxyphenyl)acetaldehyde 15. Compound **14** was treated as in the procedure used in the conversion **11** to **12**, with diisobutylaluminum hydride to afford **15** as a colorless solid in 94% yield after chromatography on silica gel with ether/hexanes as the eluent: NMR (90 MHz, $CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz), 2.16 (s, 3 H), 2.19 (s, 3 H), 3.64 (d, 2 H, J = 3.0 Hz), 3.82 (s, 3 H), 3.91 (q, 2 H, J = 7.0 Hz), 6.61 (s, 1 H), 9.65 (t, 1 H, J = 3.0 Hz); IR ($CHCl_3$) 3010, 2970, 2880, 2760, 1730, 1610, 1500, 1480, 1400, 1340, 1295, 1235, 1150, 1125, 1095, 1050, 920, 855 cm^{-1}.

Methoxy Ethoxy Bis(benzyloxy) Enol Ester 16. Compound **15** was treated, under identical conditions as was **12** in the preparation of **5**, with lithium 2,2,6,6-tetramethylpiperidide and **10** to afford **16** as a colorless solid in 71% yield after chromatography on silica gel with ether/hexanes as the eluent: mp 92.0–93.5 °C; NMR (90 MHz, $CDCl_3$) δ 1.33 (t, 3 H, J = 7.0 Hz), 2.20 (s, 3 H), 2.27 (s, 6 H), 2.20 (s, 3 H), 3.73 (s, 2 H), 3.79 (s, 3 H), 3.91 (q, 2 H, J = 7.0 Hz), 4.97 (s, 2 H), 5.10 (s, 2 H), 6.26 (d, 1 H, J = 13.5 Hz), 6.60 (s, 1 H), 6.74 (s, 1 H), 7.34 (m, 11 H); IR ($CHCl_3$) 3040, 2960, 2910, 1750, 1670, 1600, 1490, 1470, 1460, 1395, 1385, 1330, 1290, 1230, 1150, 1120, 1095, 1070, 1035, 1005, 945, 920, 850 cm^{-1}. Anal. Calcd for $C_{37}H_{40}O_6$: C, 76.51; H, 6.96. Found: C, 76.69; H, 7.02.

(Ethylenedioxyphenyl)acetic Ester 17. Catechol **7** was treated, under identical conditions as in the preparation of **8**, with potassium carbonate and 1,2-dibromoethane to provide **17** as a colorless solid in 93% yield after chromatography on silica gel with ether/hexanes as the eluent: NMR (90 MHz, $CDCl_3$) δ 1.26 (t, 3 H, J = 7.0 Hz), 2.08 (s, 3 H), 2.14 (s, 3 H), 3.52 (s, 2 H), 4.08 (q, 2 H, J = 7.0 Hz), 4.11 (s, 4 H), 6.50 (s, 1 H).

(Ethylenedioxyphenyl)acetaldehyde 18. Compound **17** was treated, under identical conditions as was **11** in the preparation **12**, with diisobutylaluminum hydride to give **18** as a colorless solid in 91% yield after chromatography on silica gel with ether/hexanes as the eluent: NMR (60 MHz, $CDCl_3$) δ 2.36 (s, 3 H), 2.43 (s, 3 H), 3.87 (d, 2 H, J = 3.0 Hz), 4.49 (s, 4 H), 6.85 (s, 1 H), 9.91 (t, 1 H, J = 3.0 Hz); IR ($CHCl_3$) 3050, 3010, 2960, 2910, 2855, 2765, 2490, 2445, 1725, 1620, 1600, 1490, 1400, 1380, 1330, 1225, 1137, 1110, 1060, 1018 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.87; H, 6.86. Found: C, 69.79; H, 6.88.

Ethylenedioxy Bis(benzyloxy) Enol Ester 20. Compound **18** was treated, under identical conditions as was **12** in the preparation of **5**, with lithium 2,2,6,6-tetramethylpiperidide and **10** to afford **20** as a colorless solid in 46% yield after chromatography on silica gel with ether/hexanes as the eluent: NMR (90 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 2.18 (s, 3 H), 2.25 (s, 3 H), 2.29 (s, 3 H), 3.71 (s, 2 H), 4.14 (s, 4 H), 4.96 (s, 2 H), 5.09 (s, 2 H), 6.21 (d, 1 H, J = 13.5 Hz), 6.53 (s, 1 H), 6.72 (s, 1 H), 7.32 (m, 11 H); IR ($CHCl_3$) 3040, 2960, 2910, 1750, 1670, 1595, 1485, 1460, 1385, 1320, 1225, 1150, 1105, 1075, 1040, 1015, 990, 950, 935, 910, 875, 870 cm^{-1}. Anal. Calcd for $C_{36}H_{36}O_6$: C, 76.56; H, 6.44. Found: C, 76.52; H, 6.50.

Ethylenedioxy Dihydroxy Enol Ester 21. Compound **20** (111 mg, 0.20 mmol) was added to a 7-mm NMR tube followed by the addition of a minimum amount of $CDCl_3$. The NMR tube was fitted with a septum and purged with argon. A 70-μL (0.50 mmol) sample of trimethylsilyl iodide was added all at once and the reaction allowed to proceed at room temperature until NMR analysis showed that the reaction was complete. Triethylamine (137 μL, 1.0 mmol) was added and the NMR tube was gently agitated for 30 min. This mixture was then diluted with ethyl acetate and washed with water which was back-extracted with ethyl acetate. The combined extracts were washed with brine and dried over sodium sulfate to provide 99 mg of crude disiloxy enol ester. This residue along with 200 mg of potassium fluoride, 10 mL of THF, and 3 mL of water was stirred at room temperature for 1 h. The THF was removed in vacuo and the residue diluted with ethyl acetate. This solution was then washed with water which was back-extracted with ethyl acetate. The combined extracts were washed with brine and dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave the crude dihydroxy enol ester which was recrystallized from benzene/

hexanes to afford 39 mg (51%) of **21** as a colorless solid: NMR (60 MHz, $CDCl_3$) δ 2.13 (s, 3 H), 2.21 (bs, 9 H), 3.72 (s, 2 H), 4.20 (s, 4 H), 6.28 (d, 1 H, J = 13.5 Hz), 6.42 (s, 1 H), 6.55 (s, 1 H), 7.20 (d, 1 H, J = 13.5 Hz); IR ($CHCl_3$) 3640, 3570, 3020, 2970, 2910, 1735, 1620, 1600, 1490, 1390, 1320, 1305, 1260, 1250, 1225, 1160, 1110, 1075, 1040, 1010, 990, 910, 855 cm^{-1}. Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.72; H, 6.30. Found: C, 68.79; H, 635.

It is likely that the yields for this reaction could be improved if the disiloxy ether was hydrolyzed by heating in methanol.[2]

***o*-Quinone Enol Ester 22.** Catechol **21** (20 mg, 0.052 mmol) was dissolved in 8 mL of dry benzene. Silver(I) oxide (120 mg, 0.52 mmol) was added, the flask purged with nitrogen, and the reaction mixture stirred at room temperature for 1 h. The silver salts were filtered from the solution, and the solvent was removed in vacuo to afford 20 mg of **22** as a red glass: NMR (60 MHz, $CDCl_3$) δ 2.05 (s, 3 H), 2.10 (bs, 9 H), 3.68 (s, 2 H), 4.22 (s, 4 H), 6.20 (s, 1 H), 6.30 (d, 1 H, J = 13.5 Hz), 6.55 (s, 1 H), 7.18 (d, 1 H, J = 13.5 Hz).

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grant CHE-79-17570.

Structure-Resonance Theory and the Kinetics of the Electrophilic Deuterium–Hydrogen Exchange in Benzenoid Hydrocarbons

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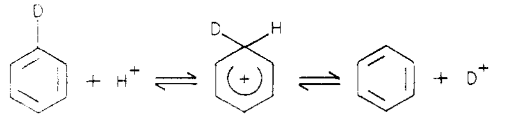
Structure-resonance theory has recently been shown to correlate and to predict various physical and chemical properties of π-electron hydrocarbons.[1,2] Thus, e.g., the theory leads to quickly obtainable quantitative predictions of bond orders, charge distribution, heats of formation, bond lengths, NMR coupling constants, and relative stabilities of ground-state species and reaction intermediates. The major advantage of this theory is its simplicity. Its application requires only an enumeration of Kekulé structures, since it has been shown that an algorithm, logarithm of the Kekulé corrected structure count,[3] gives an excellent approximation of the ground-state eigenvalues of the structure–function Hamiltonian matrix.

The purpose of this contribution is to show that the structure-resonance theory can be used to correlate the rates of both the deuterium–hydrogen and hydrogen–deuterium exchange reactions of benzenoid hydrocarbons (eq 1). The kinetic data suitable for this purpose have been published.[4-6]



(1)

Results and Discussion

In previous publications,[4,5] a correlation of the log k values of protodedeuteration with the Wheland HMO atom localization energies yielded three separate lines, depending on the type of the reaction site (benzene-like, α-naphthalene-like, and *meso*-anthracene-like positions).[5] Similar splitting has been observed in the case of deuterodeprotonation, nitration, bromination, and other electrophilic aromatic substitutions.[7,8] This splitting into three dependences was explained as due to the differences in the electronic repulsion in positions of different classes of benzenoid hydrocarbons which are not taken into account in HMO calculations.[5,8] Thus, not surprisingly, a single regression line was obtained when SCF–MO localization energies were used.[5]

Assuming that the hydrogen–deuterium exchange reactions involve the formation of a symmetrical Wheland transition intermediate (eq 1), the rates can be correlated with the differences in the resonance energy, RE, between the π-hydrocarbon substrate, ArH, and the σ-complex intermediate, $ArHD^+$. For the deuterodeprotonation and the protodedeuteration reactions, the differences in resonance energies between the reactant and the intermediate can be expressed by eq 2 and 3, respectively.

$$\Delta RE = RE_{ArHD^+} - RE_{ArH} \qquad (2)$$

$$\Delta RE = RE_{ArHR^+} - RE_{ArD} \qquad (3)$$

The resonance energy of a given species has been shown to be given by eq 4, where SC is the structure count, i.e.,

$$RE = a \ln SC \qquad (4)$$

the number of principal resonance structures of the species examined, and a is the proportionality constant (1.185).[3] Because the activation energy of a reaction is determined by the difference in the resonance stabilization of the intermediate I and the reactant R, one can write:

$$\ln k = a_0 + a_1 \ln SC_I - a_2 \ln SC_R \qquad (5)$$

The constants a_1 and a_2 can be determined by regression analysis and sensible results require that the absolute values of these two constants should not be too different. Under such conditions, eq 5 can be rewritten in the form where SC(ratio) = SC_I/SC_R. Equations of the type 5 and 6 are therefore expected to correlate with the kinetic data

$$\ln k = a_0 + a \ln SC(\text{ratio}) \qquad (6)$$

for deuterium–hydrogen exchange reactions of benzenoid hydrocarbons. The SC's for the benzenoid hydrocarbons and the corresponding σ-complex cations were determined with the coefficients of nonbonding molecular orbitals as previously described.[9,10] The results of the calculations and the rate constants used are summarized in Table I. When the data for the protodedeuteration reaction were correlated by eq 5, the following linear relationship was obtained:

$$\ln k_{D-H} = -16.707 + 9.815 \ln SC_I - 9.810 \ln SC_R \qquad (7)$$

with a correlation coefficient r = 0.973 and a standard deviation s = ±0.723. The values of the constants a_1 and a_2 in eq 7 are indeed similar, their ratio being close to unity

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