lution of **4**. The yellow solution formed this way was then transferred under dry nitrogen into a precooled NMR tube.

The Thermal Rearrangement of 4 to Bicyclo[5.1.0]octadienyliron Tricarbonyl Cation 3. When a solution of **4** was allowed to warm up to −60 °C, ^{1}H NMR signals due to ion **4** completely disappeared and were replaced by those of **3** formed quantitatively.

^{13}C NMR Spectroscopic Study. The ^{13}C NMR spectra were obtained using a Varian XL-100-15 NMR spectrometer equipped with FT accessory, spin decoupler, and a variable temperature probe. A Varian 620L computer was used to accumulate data. An external lock (fluorobenzene) was used and all chemical shifts are referred to the ^{13}C signal of the enriched (5) Me_4Si capillary.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—**1**, 12093-05-9; **3**, 41853-19-4; **4**, 41370-96-1; **5**, 45977-75-1; **10**, 12078-32-9; **11**, 12307-07-2; **12**, 46134-85-4; **13**, 49654-90-2; **14**, 46236-85-1; **15**, 63765-50-4; **16**, 61216-90-8; **17**, 63765-51-5; **18**, 63765-52-6.

References and Notes

(1) (a) Organometallic Chemistry, 15: G. A. Olah, G. K. Prakash, G. Liang, K. L. Henold, and G. B. Haigh, *Proc. Natl. Acad. Sci. U.S.A.*, in press. Address correspondence to this author at the Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, Calif.

(2) (a) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc., London*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960); (b) M. D. Rausch and B. N. Schrauzer, *Chem. Ind. (London)*, 957 (1959); (c) K. Nakamura and N. Haglhara, *Bull. Chem. Soc. Jpn.* **2**, 880 (1959); (d) B. Dicken and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961); *J. Chem. Phys.*, **37**, 2084 (1962); (e) C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1388 (1965).

(3) (a) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968); *J. Chem. Soc.*, 400 (1960); (b) F. A. Cotton, "Dynamic NMR Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975; (c) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 49 (1959).

(4) (a) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966); (b) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966); (c) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966); (d) F. A. Cotton, J. N. Faller, and A. Musco, *ibid.*, **90**, 1438 (1968); (e) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 5267 (1965); (f) F. A. L. Anet, *ibid.*, **89**, 2491 (1967); (g) A. Carbonaro, A. Greco, and G. Dall'Aota, *Tetrahedron Lett.*, 2037 (1967); (h) W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 1324 (1967); (i) M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967); (j) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967).

(5) (a) F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, **98**, 1413 (1976); (b) F. A. Cotton, D. L. Hunter, and P. LaLuerta, *ibid.*, **96**, 7926 (1974); (c) G. Rigatti, G. Boccalon, A. Accon, and G. Giacometti, *Chem. Commun.*, 1165 (1972).

(6) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

(7) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 555 (1961); *J. Chem. Soc.*, 482 (1962).

(8) (a) M. Brookhart and E. R. Davis, *J. Am. Chem. Soc.*, **92**, 7622 (1970); (b) M. Brookhart, E. R. Davis, and D. L. Harris, *ibid.*, **94**, 7853 (1972).

(9) (a) G. A. Olah, S. H. Yu, and G. Liang, *J. Org. Chem.*, **41**, 2227, 2383 (1976); (b) G. A. Olah and G. Liang, *ibid.*, **41**, 2659 (1976).

(10) G. A. Olah, G. Liang, L. A. Paquette, M. J. Broadhurst, and P. Warner, *J. Am. Chem. Soc.*, **95**, 3386 (1973).

(11) (a) L. Kruczynski and J. Takats, *J. Am. Chem. Soc.*, **96**, 932 (1974); (b) F. A. Cotton, V. W. Days, B. A. Frenz, K. I. Hardcastle, and J. M Troup, *ibid.*, **95**, 4522 (1973).

(12) (a) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 360. 1335 (1974); (b) L. Vancea, R. K. Pomeroy, and W. A. G. Graham, *J. Am. Chem. Soc.*, **98**, 1407 (1976); (c) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971); (d) H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **88**, 2710 (1966); (e) C. G. Kreiter, M. Lang, and H. Strack, *Chem. Ber.*, **108**, 1502 (1975); (f) J. Evans and J. R. Norton, *Inorg. Chem.*, **13**, 3042 (1974).

A Synthesis of 6-Hydroxy-1-benzoxepin-3,5(2*H*,4*H*)-dione

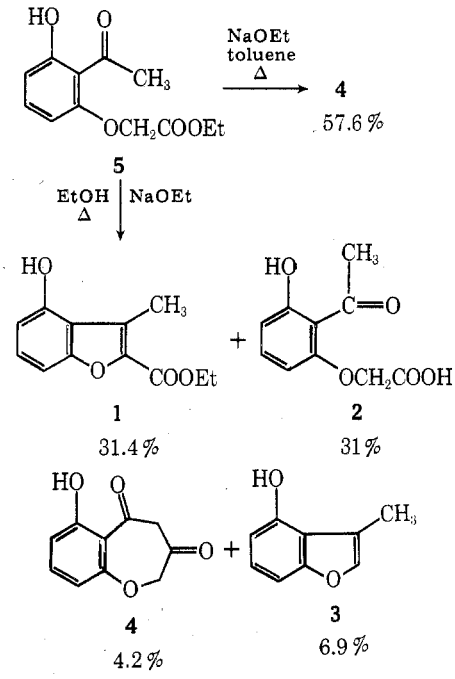
B. K. Wasson,* P. Hamel, and C. S. Rooney

Medicinal Chemistry Department, Merck Frosst Laboratories, Pointe Claire/Dorval, Quebec H9R 4P8, Canada.

Received June 2, 1977

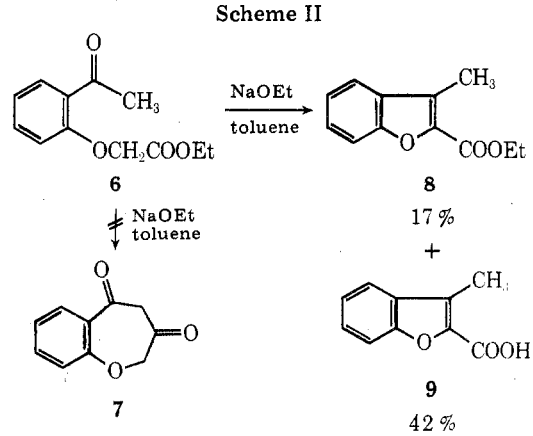
Recently, a relatively large quantity of the known ethyl 4-hydroxy-3-methyl-2-benzofurancarboxylate (**1**) was required. Repetition of Whalley's[1] procedure in a modified form afforded not only **1** in 31.4% yield, but three additional products (see Scheme I). Two of these, (2-acetyl-3-hydroxyphenoxy)acetic acid (**2**) and 4-hydroxy-3-methylbenzofuran (**3**) isolated in 31 and 6.9% yields, respectively, had been reported by Whalley.[1] Compound **3** could also be formed from **2** when the latter was heated with acetic anhydride.[1] The fourth product, identified as the hitherto unknown 6-hydroxy-1-benzoxepin-3,5(2*H*,4*H*)-dione (**4**), was isolated along with **2** and **3** after silica gel column chromatography in 4.2% yield. The assignment of structure to **4** was based on microanalysis, NMR, IR, UV, and mass spectrometry. Spectral evidence supports the diketo form rather than the enolic in both the solid state and in solution. Thus, the NMR spectrum exhibits two $-CH_2-$ peaks at δ 4.32 and 4.50 and one exchangeable proton at δ 12.31. Similar conclusions have been reported for the structure of 1-benzoxepin-3,5(2*H*,4*H*)-diones.[2-5] The pK_a of **4** is 4.83—presumably representing dissociation of the diketone function.

Scheme I



When ester **5** was allowed to react with sodium ethoxide in dry toluene, **4** was obtained in 57.6% yield. However, similar treatment of ethyl 2-(2-acetylphenoxy)acetate (**6**) gave only the benzofurans **8** and **9**, and no 1-benzoxepin-3,5(2*H*,4*H*)-dione (**7**) was observed. It thus appears that the phenolic hydroxyl plays an essential role in the formation of the benzoxepin **4**. Compound **4** remained unchanged after heating at 65 °C in sodium ethoxide–ethanol. Thus, **4** is not an intermediate

Scheme II



which in the ethanolic medium can serve as a precursor of **1**, **2**, and/or **3**.

Tyman and Pickles[2] have reported the preparation of 1-benzoxepin-3,5(2*H*,4*H*)-diones by treatment of 2-acetylphenoxyacetic esters with either ethanolic sodium ethoxide or phosphorous oxychloride in benzene. However, yields apparently were low. The high yield of **4** obtained in our work using sodium ethoxide in toluene is therefore unique, and is dependent on the acidic group ortho to the ketone combined with the aprotic solvent medium (toluene).[6] We attribute the facilitation of benzoxepin formation to the presence of an unsolvated phenolate anion which will deactivate the adjacent ketone to nucleophilic attack. Interaction of the anion formed from the methyl group, adjacent to the ketone, on the ester carbonyl can then predominate.

Experimental Section

Melting points were taken on a Thomas-Hoover Uni-melt apparatus and are uncorrected. Ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 257 spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian EM 360 spectrometer with Me_4Si as an internal reference. Mass spectral analyses were provided by Morgan-Schaffer Corp., and elemental microanalyses were carried out by Dr. C. Daessle. The pK_a determination was performed by Mr. S.-C. Ho in these Laboratories.

Cyclization of Ethyl 2-(2-Acetyl-3-hydroxyphenoxy)acetate (5) with Sodium Ethoxide in Ethanol. The compound **5**[1] (23.8 g, 0.1 mol), dissolved in 600 mL of ethanol containing 2.3 g of reacted sodium, was stirred overnight at room temperature. The solution was heated at 80 °C for 3 h and then evaporated. The residue was partitioned between ethyl ether and water. The aqueous fraction was acidified and extracted with diethyl ether, and the ethereal extract was evaporated to give 10.4 g of a brown solid. The solid was triturated with benzene to afford 6.52 g (31%) of semipure 2-acetyl-3-hydroxyphenoxyacetic acid (**2**), mp 183–188 °C. A recrystallization raised the melting point to 193–195 °C (H_2O) (lit.[7] mp 193–194.5 °C); IR (KBr) 1785, 1630, 1605, 1480, 1262, 1213 and 1120 cm^{-1}; NMR (Me_2SO-d_6) δ 2.62 (3 H, s), 4.75 (2 H, s), 6.53 (2 H, m), and 7.4 (1 H, t). Evaporation of the combined benzene and the first ethereal extracts gave 12.2 g of a solid which was chromatographed on silica gel (60–200 mesh). Elution with benzene–ethyl acetate (changing from a ratio of 1:99 to 1:1) afforded three major fractions. The first fraction of 1.02 g (6.9%) was crude 4-hydroxy-3-methylbenzofuran (**3**), which afforded needles: mp 110–112 °C (lit.[1] mp 111 °C) (C_6H_6–petroleum ether); IR (KBr) 3300 (br), 1640, 1620, 1600, 1480, 1470, 1332, 1260, 1220, 1109, 1040, 790, 746; NMR ($CDCl_3$) δ 2.34 (3 H, s), 5.03 (1 H, s) (exchanged with D_2O), 6.52 (1 H, m), 7.03 (1 H, s), and 7.2 (2 D, m). The second fraction afforded 340 mg (2.3%) of 6-hydroxy-1-benzoxepin-3,5(2*H*,4*H*)-dione (**4**): mp 139–141 °C (C_6H_6–petroleum ether); UV (EtOH) λ_{max} 217 nm (ϵ 15 100), 226 (ϵ 14 800), 266 (ϵ 10 235), and 341 (ϵ 4100); IR (KBr) 1740, 1630, 1603, 1555, 1538, 1455, 1232, 1058, 970, 790, and 740 cm^{-1}; NMR ($CDCl_3$) δ 4.32 (2 H, s), 4.50 (2 H, s), 6.78 (2 H, m), 7.45 (1 H, m), and 12.31 (1 H, s) (exchanged with D_2O); mass spectrum *m/e* 192 (M^+), 150 ($M^+ - C_2H_2O$), 121 ($M^+ - C_3H_3O_2$).

Anal. Calcd for $C_{10}H_8O_4$ (192.17): C, 62.50; H, 4.20. Found: C, 62.43; H, 4.33. pK_a = 4.83. A second crop of **4** was obtained in a 280-mg (1.9%) yield, mp 136–139 °C.

The third fraction gave 6.91 g (31.4%) of ethyl 4-hydroxy-3-methyl-2-benzofurancarboxylate (**1**): mp 157–159 °C (lit.[1] mp 155 °C) (C_6H_6–petroleum ether); IR (KBr) 3290, 1690, 1622, 1592, 1460, 1392, 1283, 1190, 1065 and 752 cm^{-1}; NMR (Me_2SO-d_6) δ 1.33 (3 H, t), 2.68 (3 H, s), 4.32 (2 H, q), 6.72 (1 H, m), 7.2 (2 H, m), and 10.28 (1 H, br) (exchanged with D_2O).

The compound **4** (19.2 mg, 0.1 mmol) dissolved in 2 mL of absolute ethanol containing 2.3 mg (0.1 mmol) of sodium was stirred at room temperature for 60 h and then heated at 65 °C for 3 h. Monitoring by TLC indicated no change. The product, isolated by acidification and evaporation, was shown by NMR analysis to be unchanged **4**.

Cyclization of Ethyl 2-(2-Acetyl-3-hydroxyphenoxy)acetate (5) with Sodium Ethoxide in Toluene. The compound **5** (476.4 mg, 2 mmol) was refluxed for 24 h in a suspension of sodium ethoxide (56.5 mg, 2.3 mmol) in 10 mL of toluene. The reaction mixture was evaporated and acidified, and the chloroform extract was washed with 5% sodium bicarbonate solution and then with water, dried (Na_2SO_4), and evaporated to give 300 mg of solid product. The solid gave 221 mg (57.6%) of **4** (C_6H_6–petroleum ether), identical to the sample described in the preceding experiment.

Cyclization of Ethyl 2-(2-Acetylphenoxy)acetate (6) with Sodium Ethoxide in Toluene. Similarly, a mixture of 11.10 g (50 mmol) of **6**,[8] sodium ethoxide (from 1.26 g of sodium), and 50 mL of toluene was refluxed for 1.5 h. The solvent was removed in vacuo and the residue partitioned between water and chloroform. The dried chloroform extract afforded 1.96 g (17.5%) of ethyl 3-methyl-2-benzofurancarboxylate (**8**), mp 48–50 °C (lit.[9] mp 49–51 °C). The aqueous extract was acidified, and the resulting solids were collected and crystallized to give 4.12 g (42.6%) of 3-methyl-2-benzofurancarboxylic acid (**9**), mp 187–190 °C (lit.[9] mp 192–194 °C).

Registry No.—**1**, 3781-69-9; **2**, 3361-22-6; **3**, 3610-15-9; **4**, 63815-26-9; **5**, 6769-65-9; **6**, 63615-27-0; **8**, 22367-82-4; **9**, 24673-56-1.

References and Notes

(1) W. B. Whalley, *J. Chem. Soc.*, 3229 (1951).
(2) J. H. P. Tyman and R. Pickles, *Tetrahedron Lett.*, 4993 (1966).
(3) (a) H. Hofmann, *Angew. Chem.*, **77**, 864 (1965). (b) H. Hofmann and H. Westernacher, *Chem. Ber.*, **102**, 205 (1969).
(4) J. R. Doherty, D. D. Keane, W. I. O'Sullivan, and E. M. Philbin, *Chem. Ind. (London)*, 586 (1969).
(5) S. Klutchko and M. Von Strandtmann, *Synthesis*, 61 (1977).
(6) An alternate route to 1-benzoxepin-3,5(2*H*,4*H*)-diones from flavanone epoxides through 3-hydroxyflavanones has been described.[3,4] Also, 1-benzoxepin-3,5(2*H*,4*H*)-dione has been prepared from 3-(bromoacetyl)chromone.[5]
(7) W. G. Scharpt (FMC Corp.), Belgium 670 764 (Jan. 31, 1966); *Chem. Abstr.*, **65**, 8876c (1966).
(8) S. K. V. Kulkarni, P. B. Sattur, and K. S. Nargund, *J. Karnatak Univ.* **2**, 69–78 (1957); *Chem. Abstr.*, **53**, 14986b (1959).
(9) B. Sila, *Rocz. Chem.* **43**, 1413–1418 (1969).

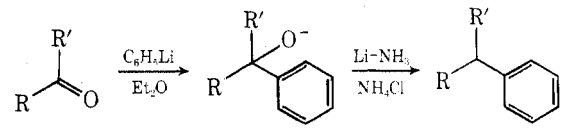
Synthesis of Aromatic Hydrocarbons and Alcohols by Tandem Phenylation–Reduction of Esters and Lactones[1]

Srisamorn T. Srisethnil[2] and Stan S. Hall*

Carl A. Olson Chemistry Laboratories, Rutgers University, Newark, New Jersey 07102

Received June 10, 1977

This laboratory has been exploring the potential applications of tandem alkylation–reduction of aromatic carbonyl systems[3] and phenylation–reduction of aldehydes and ketones[1,4] as a convenient method of preparing aromatic hydrocarbons. The method involves the lithium–ammonia–ammonium chloride reduction of a benzyl alkoxide generated in situ by alkylation. Since the entire sequence is performed in the same reaction vessel without the isolation or purification of intermediates, the total synthesis consumes only a few hours and the isolated yield of the product is usually good. Herein we extend the application of this tandem phenylation–reduction procedure to esters and lactones.



Since subjecting esters and lactones to an excess of phenyllithium results in the formation of a benzyl alkoxide (a 1,1-diphenyl 1-alkoxide), these carbonyl systems seemed appropriate starting materials for the synthesis of 1,1-diphenyl hydrocarbons and alcohols using this tandem sequence. The results are listed in Table I. Esters yield the corresponding 1,1-diphenyl hydrocarbons. Two examples are given. Phenylation–reduction of ethyl acetate (**1**) yielded 1,1-diphenylethane (**9**) and methyl benzoate (**2**) yielded triphenylmethane (**10**).

Phenylation–reduction of lactones, on the other hand, yields the corresponding diphenyl alcohols. For example, γ-butyrolactone (**3**) yielded 4,4-diphenyl-1-butanol (**11**). Related