ppm) as the second intermediate. Furthermore, by treatment of 1 with borane–THF in a 1:2 ratio, 3 equiv of hydrogen was evolved, and only 19% of hydride uptake in 0.5 h and 23% of reduction in 1 h were achieved (Table I and Scheme I). The ^{11}B NMR of the partially precipitated reaction aliquot showed two compounds corresponding to 3 (+26.1 ppm) and 4 (+2.9 and +19.2 ppm).[8] These experiments clearly indicate that at 0 °C the α-hydrogen abstraction is more predominant than the reduction. The reduction proceeding through the intermediate 4 is exceptionally slow and essentially stops the reaction.

Consequently, to control the α-hydrogen abstraction from 1 by borane–THF, the reaction was carried out at a lower temperature. Addition of BH_3·THF to 1 in a ratio of 8:3 at −20 °C resulted in the evolution of 2 equiv of hydrogen and consumption of 37% active hydride for reduction in 5 min. It appeared that the course of the reaction at −20 °C was significantly faster in the first 5 min than at 0 °C. This indicates to us that the reduction via 2 is probably much faster than through the intermediate 4 formed by α-hydrogen abstraction from 2.

In conclusion, an important new intermediate formed by reduction of 1 with borane–THF was identified as the relatively stable cyclic 2. From this intermediate a second (4) is formed by α-hydrogen abstraction. This can be suppressed by lowering the temperature to −20 °C. Intermediate 4 appears to be more resistant to further reduction than 2.

Experimental Section

^{11}B FT-NMR and ^{1}H FT-NMR spectra were recorded on a Jeol FX-90Q FT-NMR spectrometer. All ^{1}H chemical shifts are relative to tetramethylsilane (δ 0), and ^{11}B chemical shifts are relative to boron trifluoride etherate (δ 0). FT-IR spectra were recorded on FX-6160 FT-IR spectrometer. All glassware was dried thoroughly in a drying oven and cooled under a dry stream of nitrogen. All reduction experiments were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer the solution. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was dried with excess lithium aluminum hydride, distilled under nitrogen immediately prior to use. Borane–THF was the commercial product and standardized by hydrolyzing a 1 mL aliquot of the solution with glycerine–water–THF mixture and measuring the hydrogen evolved. Carboxylic acids were the commercial product of the highest purity.

Procedure for the Rate Study. The reduction of phenylmalonic acid is representative. Two 50-mL round-bottom flasks with side arm were dried in an oven and cooled down in a dry nitrogen atmosphere. The first flask was equipped with a rubber syringe cap, a magnetic stirring bar, and a reflux condenser, connected to a gas buret. Then 3 mL (1.5 mmol) of a 0.5 M solution of phenylmalonic acid was injected into the reaction flask, followed by 4.5 mL of dry THF (the resulting solution contained 1.0 M in hydride and 0.25 M in functional group). The flask was immersed in an ice bath and cooled to 0 °C. Then 4.52 mL (12 mmol of hydride) of 0.89 M borane solution in THF was added slowly. There was evolved 110 mL (4.33 mmol, 1.44 mmol/FG) of hydrogen in 0.25 h. The rate of hydrogen evolved was followed with time. The results are summarized in Table I.

The second reaction flask was prepared in the same manner. Aliquots (2.0 mL) were withdrawn at various time intervals and analyzed by hydrolysis. A blank experiment was performed in which THF was substituted for the acid. From the difference, the number of millimoles of hydride used for reduction per millimole of acid and hence the percentage of reaction was calculated. The results are given in Table I. The isolation of the diol was described in a previous study.[4]

(Phenylmalonoxy)borane. The apparatus is the same as that described previously. In a 50-mL, round-bottom flask was placed 3 mL (1.5 mmol) of 0.5 M solution of phenylmalonic acid followed by 4.5 mL of dry THF. The mixture was cooled to 0 °C, and then 1.3 mL of 0.89 M BH_3·THF (1.5 mmol) was slowly added. Hydrogen evolution (72 mL, 2.84 mmol) was over in 1.5 h. The glass apparatus was weighed. A small piece of vacuum tubing was attached to the connecting tube. It was then immersed in a water bath at room temperature and connected to a vaccum setup. The flask was then opened slowly to the vaccum, and the weight change was noted with time. A white, crystalline solid whose weight corresponds to $PhCH(CO_2)_2BH$, 0.28 g (98%), mp 159–161 °C: IR (THF) 2470 (br s), 1725 (sh), 1702 (s), 1600 (s), 1560 (w), 1502 (s), 1330 (m), 1290 (vs), 1090 (m), 990 (m), 770 (m), 690 (m) cm $^{-1}$; ^{1}H NMR ($CDCl_3$) δ 4.61 (s, 1 H, benzylic) and 7.36 (s, 5 H, Ar); ^{11}B NMR (THF) +2.98 ppm.

Registry No. 1, 2613-89-0; 2, 109306-89-0; 3, 109306-90-3; 4, 109306-91-4; 5, 109306-92-5; benzoic acid, 65-85-0; phenylacetic acid, 103-82-2.

(8) It appears that the second intermediate, 4, slowly precipitates out of the solution during the course of the reaction, as indicated by the decrease in the ^{11}B NMR resonances of 4 and the increase in the amount of precipitate present.

Hypervalent Iodine Oxidation of *p*-Alkoxyphenols and Related Compounds: A General Route to *p*-Benzoquinone Monoacetals and Spiro Lactones

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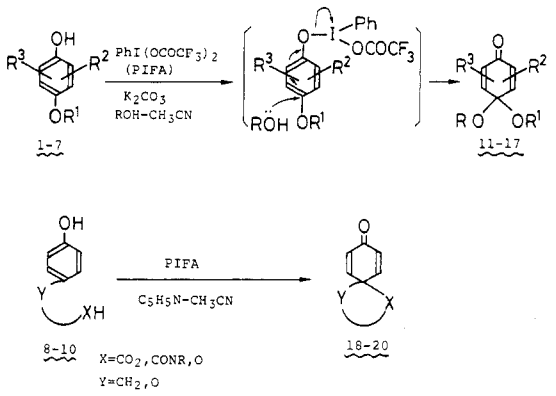
Quinone monoacetals are potentially attractive compounds as regiospecific quinone equivalents in organic synthesis and the chemistry of the acetals is summarized in recent reviews.[1] They serve as precursors to various types of natural products such as tropolones,[2] ryanodol,[3] α-tocopherol,[4] and anthracyclines.[5] These quinones are generally prepared by (i) chemical oxidation of 4-alkoxy- or 4-(aryloxy)phenols with oxidizing reagents such as copper(II) species,[6] ceric salts,[7] and thallium(III) nitrate (TTN),[8] (ii) electrochemical oxidation of *p*-methoxyphenols[9] or their trimethylsilyl ethers,[10] and (iii) monohydrolysis of quinone bisacetals.[1b,11] Althouth the first method (i) is the most facile and shortest route to quinone monoacetals of these methods, it often employs highly

(1) (a) Fujita, S. *Yuki Gosei Kagaku Kyokaishi* **1982**, *40*, 307. (b) Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74.
(2) (a) Evans, D. A.; Hart, D. J.; Koelsch, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 4593. (b) Evans, D. A.; Tanis, S. P.; Hart, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 5813. (c) Mak, C.-P.; Büchi, G. *J. Org. Chem.* **1981**, *46*, 1.
(3) Deslongchamps, P. *Pure Appl. Chem.* **1977**, *49*, 1329.
(4) Cohen, N.; Lopresti, R. J.; Saucy, G. *J. Am. Chem. Soc.* **1979**, *101*, 6710.
(5) (a) Chenard, B. L.; Anderson, D. K.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1980**, 932. (b) Swenton, J. S.; Freskos, J. N.; Morrow, G. W.; Sercel, A. D. *Tetrahedron* **1984**, *40*, 4625. (c) Keay, B. A.; Rodrigo, R. *Tetrahedron* **1984**, *40*, 4597. (d) Becker, A. M.; Irvine, R. W.; McCormick, A. S.; Russell, R. A.; Warrener, R. N. *Tetrahedron Lett.* **1986**, *27*, 3431.
(6) Hewitt, D. G. *J. Chem. Soc. C* **1971**, 2967.
(7) Dürckheimer, W.; Cohen, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 4388.
(8) (a) McKillop, A.; Perry, D. H.; Edwards, M.; Antus, S.; Farkas, L.; Nógrádi, M.; Taylor, E. C. *J. Org. Chem.* **1976**, *41*, 282. (b) Crouse, D. J.; Wheeler, M. M.; Goemann, M.; Tobin, P. S.; Basu, S. K.; Wheeler, D. M. S. *J. Org. Chem.* **1981**, *46*, 1814.
(9) (a) Nilsson, A.; Ronlân, A.; Parker, V. D. *Tetrahedron Lett.* **1975**, 1107. (b) Foster, C. H.; Payne, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 2834. (c) Chen, C.-P.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1985**, 1291.
(10) Stewart, R. F.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 4999.
(11) (a) Buchanan, G. L.; Raphael, R. A.; Taylor, R. *J. Chem. Soc., Perkin Trans 1* **1973**, 373. (b) Henton, D. R.; McCreery, R. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 369.

0022-3263/87/1952-3927$01.50/0

Scheme I



toxic oxidants and the yields are generally moderate to low. Büchi and Mak reported[12] an improved method for the benzoquinone monoacetals using less toxic 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or ferric chloride in the presence of suspended potassium bicarbonate in methanol and successfully applied it to the synthesis of neolignans[13] and gymnomitrol.[14] However, the reactivity of these oxidants is still not so active and is dependent on the substrate used. In a continuation of our study on the hypervalent iodine compounds,[15] we now report here potentially efficient oxidant, phenyliodosyl bis(trifluoroacetate) (PIFA),[16] which can react with various types of *p*-alkoxyphenols (**1–7**) to give the *p*-benzoquinone monoacetals (**11–17**) in excellent yields under mild conditions.

A typical experimental procedure is as follows for the reaction of 3,4-(methylenedioxy)phenol (**1**) with PIFA. To a solution of **1** in anhydrous methanol containing powdered potassium carbonate was added a solution of an equimolar amount of PIFA in anhydrous acetonitrile. The mixture was stirred for 10 min at room temperature to give **8a** in a quantitative yield. Oxidation of other phenols (**2–7**) with PIFA proceeded rapidly under similar conditions, and the corresponding pure *p*-benzoquinone monoacetals (**11–17**) were readily obtained in excellent yields. Unsymmetrical monoacetals of *p*-benzoquinones were also obtained in high yields (runs 1–3 and 9–11). The result of **7** is quite different from that observed in the oxidation with TTN, which gives the symmetrical dimethyl acetal caused by a transacetalization of the initially formed unsymmetrical monoacetal with methanol under the reaction conditions.[8] The oxidation was extended to intramolecular ipso-trapping by some nucleophiles such as carboxy, amido, and hydroxy groups, leading to the corresponding spiro compounds (**18–20**) (Scheme I).[17] All known products were identified by comparison with authentic samples and new compounds were characterized by microanalyses and IR and ^{1}H NMR spectral data. The reaction conditions, products, and yields are listed in Table I.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were obtained on a JASCO HPIR-102 spectrophotometer. ^{1}H NMR spectra were recorded at a Hitachi R-22 (90 MHz) spectrometer using Me_4Si as an internal standard. Low- and high-resolution mass spectra were obtained with a JEOL JMS D-300 instrument, with a direct-inlet system at 70 eV. For column chromatography, E. Merck silica gel (0.063–0.200 nm, 70–230 mesh AS7M) was used. The known phenols were prepared by the reported methods: **2**,[18] **3**,[13] **4**,[14] **5**[18] **9**.[19] PIFA and other starting phenols (**1**, **6–8**, **10**) are commercially available.

General Procedure for the Oxidation of Para-Substituted Phenols 1–10. To a stirred solution of para-substituted phenol **1–7** (1 mmol) and powdered potassium carbonate (2 mmol) in anhydrous alcohol (4 mL) at 0 °C to room temperature was added a solution of PIFA (1 mmol) in acetonitrile (2 mL). The mixture was stirred for 10 min under the same conditions, diluted with water, and extracted with ether. The organic layer was washed with saturated aqueous sodium chloride solution, dried over magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane–ethyl acetate to yield a pure *p*-benzoquinone monoacetal. Oxidation of para-substituted phenols **8a,b**, **9**, and **10** was carried out in acetonitrile in the presence of pyridine instead of potassium carbonate.

4-Methoxy-3,4-(methylenedioxy)cyclohexa-2,5-dienone (11a). This (82 mg) was obtained from **1** (69 mg, 0.5 mmol), PIFA (215 mg, 0.5 mmol), and K_2CO_3 (138 mg, 1 mmol) in methanol–acetonitrile as colorless crystals. Recrystallization from ethyl aceate–hexane gave pure **11a**: mp 72–74 °C (lit.[8a] mp 56–57 °C); IR ($CHCl_3$) 1675, 1655, 1610 cm^{-1}; NMR ($CDCl_3$) δ 6.99 (d, 1 H, J = 10 Hz, C_5-H), 6.36 (dd, 1 H, J = 10 and 2 Hz, C_6-H), 5.76 (s, 1 H, $CH_2 \times {}^1/_2$), 5.71 (s, 1 H, $CH_2 \times {}^1/_2$), 5.67 (d, 1 H, J = 2 Hz, C_2-H), 3.39 (s, 3 H, OCH_3). Anal. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 56.84; H, 4.75.

4-Ethoxy-3,4-(methylenedioxy)cyclohexa-2,5-dienone (11b). This (180 mg) was obtained from **1** (1 mmol), PIFA (1 mmol), and K_2CO_3 (2 mmol) in ethanol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **11b**: mp 57–58 °C (lit.[8a] mp 57–59 °C); IR ($CHCl_3$) 1675, 1650, 1610 cm^{-1}; NMR ($CDCl_3$) δ 6.85 (d, 1 H, J = 10 Hz, C_5-H), 6.18 (dd, 1 H, J = 10 and 2 Hz, C_6-H), 5.64 (s, 1 H, $OCH_2O \times {}^1/_2$), 5.58 (s, 1 H, $OCH_2O \times {}^1/_2$), 5.52 (d, 1 H, J = 2 Hz, C_2-H), 3.8–3.4 (m, 2 H, OCH_2CH_3), 1.17 (t, 3 H, J = 7 Hz, OCH_2CH_3).

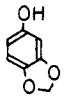
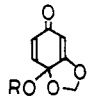
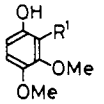
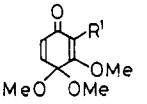
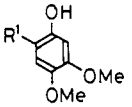
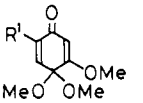
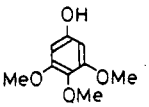
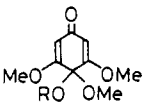
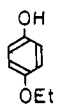
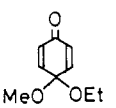
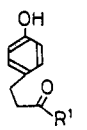
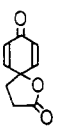
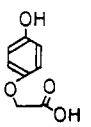
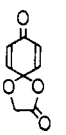
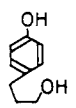
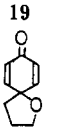
4-Isopropoxy-3,4-(methylenedioxy)cyclohexa-2,5-dienone (11c). This (157 mg) was obtained from **1** (1 mmol), PIFA (1 mmol), and K_2CO_3 (2 mmol) in isopropyl alcohol–acetonitrile as a colorless syrup: IR ($CHCl_3$) 1680, 1645, 1610 cm^{-1}; NMR ($CDCl_3$) δ 6.89 (d, 1 H, J = 10 Hz, C_5-H), 6.16 (dd, 1 H, J = 10 and 2 Hz, C_6-H), 5.77 (s, 1 H, $OCH_2O \times {}^1/_2$), 5.58 (s, 1 H, $OCH_2O \times {}^1/_2$), 5.39 (d, 1 H, J = 2 Hz, C_2-H), 4.01 (m, 1 H, CH<), 1.19 (d, 3 H, J = 6 Hz, $CHCH_3$), 1.13 (d, 3 H, J = 6 Hz, $CHCH_3$); exact mass calcd for $C_{10}H_{12}O_4$ 196.0733, found 196.0718.

3,4,4-Trimethoxycyclohexa-2,5-dienone (12). This (165 mg) was obtained from **2** (154 mg, 1 mmol), PIFA (1 mmol), and K_2CO_3 (2 mmol) in methanol–acetonitrile as colorless crystals. Recrystallization from ether–hexane gave pure **12**: mp 61–63 °C (lit.[12] mp 61 °C); IR ($CHCl_3$) 1665, 1630, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.60 (d, 1 H, J = 10 Hz, C_5-H), 6.29 (dd, 1 H, J = 10 and 2 Hz, C_6-H), 5.64 (d, 1 H, J = 2 Hz, C_2-H), 3.83 (s, 3 H, C_3-OCH_3), 3.33 (s, 6 H, C_4-OCH_3 × 2).

2-Allyl-3,4,4-trimethoxycyclohexa-2,5-dienone (13). This (92 mg) was obtained from **3** (93 mg, 0.48 mmol), PIFA (0.48 mmol), and K_2CO_3 (0.96 mmol) in methanol–acetonitrile as a pale yellow syrup:[12,13] IR ($CHCl_3$) 1665, 1630, 1605 cm^{-1}; NMR ($CDCl_3$)

(12) Büchi, G.; Chu, P.-S.; Hoppmann, A.; Mak, C.-P.; Pearce, A. *J. Org. Chem.* **1978**, *43*, 3983.
(13) (a) Büchi, G.; Mak, C.-P. *J. Am. Chem. Soc.* **1977**, *99*, 8073. (b) Büchi, G.; Chu, P.-S. *J. Org. Chem.* **1978**, *43*, 3717.
(14) (a) Büchi, G.; Chu, P.-S. *J. Am. Chem. Soc.* **1979**, *101*, 6767; (b) *Tetrahedron* **1981**, *37*, 4509.
(15) (a) Tamura, Y.; Chun, M.-W.; Inoue, K.; Minamikawa, J. *Synthesis* **1978**, 822. (b) Tamura, Y.; Shirouchi, Y.; Haruta, J. *Synthesis* **1984**, 231. (c) Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. *Chem. Pharm. Bull.* **1985**, *33*, 1097. (d) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *Tetrahedron Lett.* **1985**, *26*, 3837. (e) Tamura, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Kita, Y. *Chem. Pharm. Bull.* **1987**, *35*, 570.
(16) For reviews on hypervalent iodine reagents, see: (a) Varvoglis, A. *Synthesis* **1984**, 709. (b) Ochiai, M.; Nagao, Y. *Yuki Gosei Kagaku Kyokaishi* **1986**, *44*, 660. (c) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. For recent researches, see: (a) Moriarty, R. M.; Prakash, O.; Duncan, M. P.; Vaid, R. K.; Musallam, H. A. *J. Org. Chem.* **1987**, *52*, 150. (b) Moriarty, R. M.; Engerer, S. C.; Prakash, O.; Prakash, I.; Gill, U. S.; Freeman, W. A. *J. Org. Chem.* **1987**, *52*, 153.
(17) Similar spiro lactone formation was reported in the thermolysis of (4-azidophenyl)propionic and -butyric acids, see: Abramovitch, R. A.; Hawi, A.; Rodrigues, J. A. R.; Trombetta, T. R. *J. Chem. Soc., Chem. Commun.* **1986**, 283.
(18) Godfrey, I. M.; Sargent, M. V.; Elix, J. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1353.
(19) Sobotka, H.; Austin, J. *J. Am. Chem. Soc.* **1952**, *74*, 3813.

Table I. Oxidation of *p*-Alkoxyphenols and Related Compounds with Phenyliodosyl Bis(trifluoroacetate) (PIFA)

runs	starting materials	conditions	products	yields,[a] %
1	 **1**	$MeOH/CH_3CN$	 **11a** (R = Me)	83
2	**1**	$EtOH/CH_3CN$	**11b** (R = Et)	99
3	**1**	*i*-PrOH/CH_3CN	**11c** (R = *i*-Pr)	80
4	 **2** (R^1 = H)	$MeOH/CH_3CN$	 **12** (R^1 = H)	90
5	**3** (R^1 = allyl)	$MeOH/CH_3CN$	**13** (R^1 = allyl)[b]	85
6	 **4** (R^1 = Me)	$MeOH/CH_3CN$	 **14** (R^1 = Me)[c]	85
7	**5** (R^1 = OMe)	$MeOH/CH_3CN$	**15** (R^1 = OMe)	86
8	 **6**	$MeOH/CH_3CN$	 **16a** (R = Me)	quant
9	**6**	$EtOH/CH_3CN$	**16b** (R = Et)	quant
10	**6**	*i*-PrOH/CH_3CN	**16c** (R = *i*-Pr)	97
11	 **7**	$MeOH/CH_3CN$	 **17**	90
12	 **8a** (R^1 = OH)	CH_3CN	 **18**	86
13	**8b** (R^1 = $NHCH_2C_6H_5$)	CH_3CN	**18**	69
14	 **9**	CH_3CN	 **19**	80
15	 **10**	CH_3CN	 **20**	59

[a] Yields of products isolated by column chromatography are given. [b] The product is known as the key intermediate for neolignan.[13] [c] The product is known as the key intermediate for gymnomitrol.[14]

δ 6.38 (d, 1 H, *J* = 10 Hz, C_5-H), 6.27 (d, 1 H, *J* = 10 Hz, C_6-H), 6.1–5.5 (m, 1 H, C*H*=CH_2), 5.1–4.8 (m, 2 H, CH=C*H*$_2$), 4.15 (s, 3 H, C_3-OCH_3), 3.31 (s, 6 H, C_4-OCH_3 × 2), 3.2–3.0 (m, 2 H, CH_2); exact mass calcd for $C_{12}H_{16}O_4$ 224.1046, found 224.1043.

2-Methyl-4,4,5-trimethoxycyclohexa-2,5-dienone (14). This (84 mg) was obtained from **4** (84 mg, 0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in methanol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **14**: mp 101–101.5 °C (lit.[14] mp 103–104 °C); IR ($CHCl_3$) 1675, 1640, 1620 cm^{-1}; NMR ($CDCl_3$) δ 6.32 (br d, 1 H, *J* = 1 Hz, C_3-H), 5.61 (s, 1 H, C_6-H), 3.81 (s, 3 H, C_5-OCH_3), 3.30 (s, 6 H, C_4-OCH_3 × 2), 1.94 (d, 3 H, *J* = 1 Hz, =CCH_3).

2,4,4,5-Tetramethoxycyclohexa-2,5-dienone (15). This (92 mg) was obtained from **5** (92 mg, 0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in methanol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate gave pure **15**: mp 155–157 °C (lit.[12] mp 158–159 °C); IR ($CHCl_3$) 1665, 1650, 1620 cm^{-1}; NMR ($CDCl_3$) 5.61 (s, 1 H, C_3-H), 5.38 (s, 1 H, C_6-H), 3.83 (s, 3 H, C_5-OCH_3), 3.72 (s, 3 H, C_2-OCH_3), 3.30 (s, 6 H, C_4-OCH_3 × 2).

3,4,4,5-Tetramethoxycyclohexa-2,5-dienone (16a). This (106 mg) was obtained from **6** (92 mg, 0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in methanol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **16a**: mp 121.5–123 °C (lit.[8a] no physical and spectral data); IR ($CHCl_3$) 1665, 1630, 1605 cm^{-1}; NMR ($CDCl_3$) δ 5.59 (s, 2 H, C_2- and C_6-H), 3.78 (s, 6 H, C_3- and C_5-OCH_3), 3.25 (s, 6 H, C_4-OCH_3 × 2). Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 55.74; H, 6.58.

4-Ethoxy-3,4,5-trimethoxycyclohexa-2,5-dienone (16b). This (114 mg) was obtained from **6** (0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in ethanol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **16b**: mp 103–103.5 °C (lit.[8a] no physical and spectral data); IR ($CHCl_3$)

1660, 1630, 1605 cm^{-1}; NMR ($CDCl_3$) δ 5.57 (s, 2 H, C_2- and C_6-H), 3.78 (s, 6 H, C_3- and C_5-OCH_3), 3.40 (q, 2 H, J = 7 Hz, OCH_2CH_3), 3.24 (s, 3 H, C_4-OCH_3), 1.21 (t, 3 H, J = 7 Hz, OCH_2CH_3). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.54; H, 7.20.

4-Isopropoxy-3,4,5-trimethoxycyclohexa-2,5-dienone (16c). This (117 mg) was obtained from **6** (0.5 mmol), PIFA (0.5 mmol), and K_2CO_3 (1 mmol) in isopropyl alcohol–acetonitrile as colorless crystals. Recrystallization from ethyl acetate–hexane gave pure **16c**: mp 125.5–127 °C (lit.[8a] no physical and spectral data); IR ($CHCl_3$) 1660, 1630, 1600 cm^{-1}; NMR ($CDCl_3$) δ 5.58 (s, 2 H, C_2- and C_6-H), 4.1–3.7 (m, 1 H, C*H*<), 3.77 (s, 6 H, C_3- and C_5-OCH_3), 3.20 (s, 3 H, C_4-OCH_3), 1.12 (d, 6 H, J = 6 Hz, $CHMe_2$); exact mass calcd for $C_{12}H_{18}O_5$ 242.1153, found 242.1153.

4-Ethoxy-4-methoxycyclohexa-2,5-dienone (17). This (151 mg) was obtained from **7** (138 mg, 1 mmol), PIFA (1 mmol), and K_2CO_3 (2 mmol) in methanol–acetonitrile as a colorless syrup: IR ($CHCl_3$) 1690, 1675, 1640 cm^{-1}; NMR ($CDCl_3$) δ 6.79 (d, 2 H, J = 10 Hz, C_3- and C_5-H), 6.22 (d, 2 H, J = 10 Hz, C_2- and C_6-H), 3.62 (q, 2 H, J = 7 Hz, OCH_2CH_3), 3.34 (s, 3 H, C_4-OCH_3), 1.22 (t, 3 H, J = 7 Hz, OCH_2CH_3); exact mass calcd for $C_9H_{12}O_3$ 168.0787, found 168.0798.

1-Oxaspiro[4,5]deca-6,9-diene-2,8-dione (18). (i) This (142 mg) was obtained from **8a** (166 mg, 1 mmol) and PIFA (1 mmol) in acetonitrile as colorless crystals. Recrystallization from benzene–hexane gave pure **18**: mp 106.5–108 °C (lit.[20] mp 100–102 °C, lit.[21] mp 106 °C); IR ($CHCl_3$) 1785, 1675, 1635 cm^{-1}; NMR ($CDCl_3$) δ 6.84 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.24 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 2.9–2.2 (m, 4 H, $CH_2 \times 2$). (ii) This (53 mg) was obtained from **8b** (121 mg, 0.47 mmol), PIFA (0.47 mmol), and pyridine (0.16 mL) in acetonitrile.

1,4-Dioxaspiro[4,5]deca-6,9-diene-2,8-dione (19). This (134 mg) was obtained from **9** (168 mg, 1 mmol) and PIFA (1 mmol) in acetonitrile as pale yellow crystals; mp 57–60 °C. Recrystallization from benzene–pentane gave pure **19** as colorless needles: mp 66–67 °C (lit.[22] mp 62–64 °C); IR ($CHCl_3$) 1820, 1680, 1640 cm^{-1}; NMR ($CDCl_3$) δ 6.71 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.28 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 4.46 (s, 2 H, CH_2).

1-Oxaspiro[4,5]deca-6,9-dien-8-one (20). This (89 mg) was obtained from **10** (152 mg, 1 mmol), PIFA (1 mmol), and pyridine (0.3 mL) in acetonitrile as a syrup:[23] IR ($CHCl_3$) 1690, 1670, 1630 cm^{-1}; NMR ($CDCl_3$) δ 6.76 (d, 2 H, J = 10 Hz, C_6- and C_{10}-H), 6.08 (d, 2 H, J = 10 Hz, C_7- and C_9-H), 4.06 (t, 2 H, J = 6 Hz, CH_2), 2.4–2.0 (m, 4 H, $CH_2 \times 2$); exact mass calcd for $C_9H_{10}O_2$ 150.0678, found 150.0677.

Registry No. **1**, 533-31-3; **2**, 2033-89-8; **3**, 66967-26-8; **4**, 72312-07-3; **5**, 20491-91-2; **6**, 642-71-7; **7**, 622-62-8; **8a**, 501-97-3; **8b**, 74454-78-7; **9**, 1878-84-8; **10**, 10210-17-0; **11a**, 57197-23-6; **11b**, 57197-24-7; **11c**, 109183-15-5; **12**, 64701-03-7; **13**, 66967-27-9; **14**, 72312-08-4; **15**, 67271-97-0; **16a**, 57197-13-4; **16b**, 57197-20-3; **16c**, 57197-21-4; **17**, 73010-52-3; **18**, 4572-26-3; **19**, 4385-47-1; **20**, 67856-28-4; $PhI(OCOCF_3)_2$, 2712-78-9.

(20) Schweizer, J.; Lattrell, R.; Hecker, E. *Experientia* **1975**, *31*, 1267.
(21) Scott, A. I.; Dodson, P. A.; McCapra, F.; Meyers, M. B. *J. Am. Chem. Soc.* **1963**, *85*, 3702.
(22) Hunter, N. R.; Wang, P. M.-C. *Synth. Commun.* **1982**, *12*, 427.
(23) Goosen, A.; McCleland, C. W. *J. Chem. Soc., Perkin Trans 1* **1978**, 646.

New Syntheses of Acridin-9-ones, Benzo[*c*]quinolizin-6-ones, Pyrrolo[1,2-*a*]quinoline-1,5-diones, and Some Related Tetracyclic Compounds

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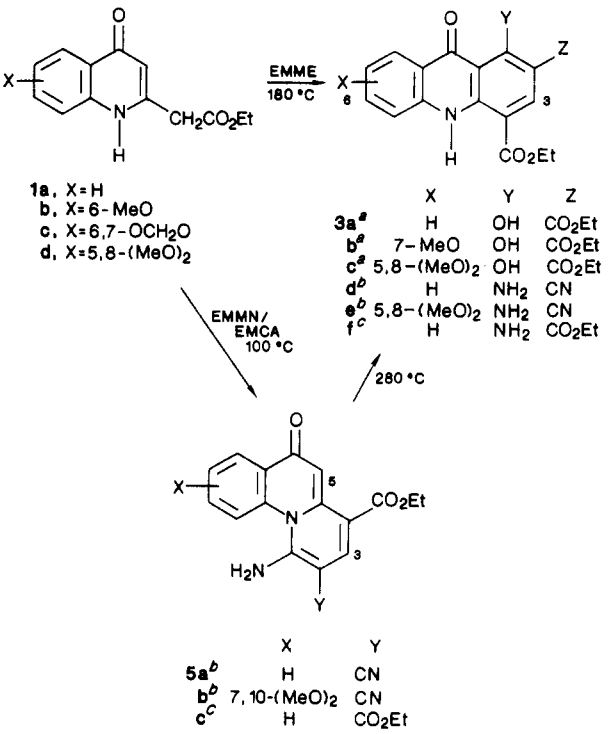
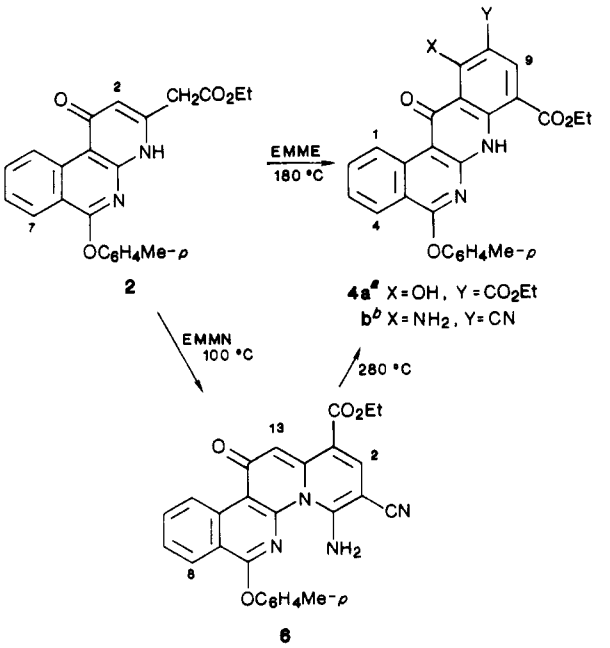
In work on possible DNA interacalating heterocycles, we were interested in the products resulting from annulation of the acetic esters **1** (Scheme I) and **2** (Scheme II).

Scheme I



[a] From EMME. [b] From EMMN. [c] From EMCA.

Scheme II



[a] From EMME. [b] From EMMN.

Compounds **1** were prepared from the anilines and diethyl 3-oxoglutarate, by an improvement on a published Conrad–Limpach synthesis.[1] The tricyclic ester **2** was obtained from 1-(*p*-methylphenoxy)isoquinolin-3-amine.[2]

Condensation reactions were then carried out with diethyl(ethoxymethylene)malonate (EMME), (ethoxymethyl)malononitrile (EMMN), ethyl (ethoxymethylene)cyanoacetate (EMCA), and diethyl acetylenedicarboxylate (DEAD).

(1) Kaslow, C. E.; Nix, S. J. *J. Org. Chem.* **1951**, *16*, 895.
(2) Deady, L. W.; Werden, D. M. *Aust. J. Chem.* **1986**, *39*, 667.

0022-3263/87/1952-3930$01.50/0