In summary, the oxypyrylium zwitterion appears to be a versatile synthon for cycloaddition to seven-,[2] eight- and ten-membered carbocyclic rings. Furthermore, the synthetic value of the initial adducts lies in their multiple functionality and the ether-bridged rigidity for stereocontrol, as demonstrated by the test reactions reported here.

Experimental Section

General. Details are described in the preceding paper.[2] Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Dichloromethane (from phosphorus pentoxide) and tetrahydrofuran (from lithium aluminum hydride) were distilled prior to use under nitrogen.

Synthesis of 3,12-Dioxatricyclo[5.3.1.1.^{2,6}]dodeca-4,8-diene-10,11-dione (3). A. From Pyranose 1 (R = $COCH_3$). To a rapidly stirred dichloromethane (20 mL) solution of 2-acetoxy-1-oxacyclohex-3-en-5-one[9] (1, R = $COCH_3$, 1.6 g, 10.2 mmol) at 0 °C under a nitrogen atmosphere was added an equimolar amount of triethylamine. After warming to room temperature over 3 h, it was stirred overnight. Concentration under reduced pressure, followed by column chromatography on silica gel with dichloromethane/ethyl acetate (6:1), gave 675 mg (69% yield) of dimer 3 as a white solid: mp 143–147 °C; NMR (CD_3CN–Me_2SO-d_6), Table I; IR ($CDCl_3$) 1770, 1690 cm^{-1}; mass spectrum, m/e 192 (M^+).

B. From Pyranose 1 (R = $COCF_3$). To 113.6 mg (1 mmol) of pyranose 1 (R = H)[9] in dichloromethane (3 mL) at −78 °C under a nitrogen atmosphere was added 0.14 mL (1 mmol) of triethylamine. This solution was added to 0.14 mL (1 mmol) of trifluoroacetic anhydride in 2 mL of dichloromethane at −78 °C via a double tipped cannula. After 15 min, 0.14 mL (1 mmol) of triethylamine was added dropwise to the above reaction mixture. The resulting solution was warmed to −10 °C over 5.5 h and then concentrated in vacuo. The residue was dissolved in ethyl acetate, washed with water and brine, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave 62.8 mg (66% yield) of dimer 3.

Synthesis of 11,12-Dioxatricyclo[5.3.1.1.^{2,6}]dodeca-4,8-diene-3,10-dione (5). A chloroform solution (1 mL) of dimer 3 (203 mg, 1.04 mmol) was sealed into a dried pyrolysis tube and then immersed for 7 h in an oil bath maintained at ~141 °C. After cooling, the heterogeneous reaction mixture was filtered through Celite. Upon concentration of the filtrate in vacuo, 169 mg (83% yield) of dimer 5 was obtained. Column chromatography on silica gel with dichloromethane/ethyl acetate (6:1) afforded pure dimer 5 as a white solid, mp 200–205 °C. Dimer 5 could also be prepared by refluxing dimer 3 in xylene under a nitrogen atmosphere overnight. Removal of the solvent under reduced pressure and chromatography as above gave pure dimer 5: NMR (CD_3CN), Table I; IR (CH_2Cl_2) 1690 cm^{-1}; mass spectrum, m/e 192 (M^+). Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.63; H, 4.23.

Synthesis of 8-Methyl-11,12-dioxatricyclo[5.3.1.1^{2,6}]dodec-4-ene-2,10-dione (8). A 0.084 M THF solution of lithium dimethylcuprate (prepared by adding 0.58 mL of 2.87 M methyllithium–ether solution to 171.8 mg (0.84 mmol) of cuprous bromide–dimethyl sulfide complex[10] in 10 mL of anhydrous THF at −70 °C) was added to 160.6 mg (0.84 mmol) of dimer 5 in THF (10 mL) at −70 °C under a nitrogen atmosphere. After 1.5 h, the cloudy yellow reaction mixture was removed from the low-temperature bath and immediately quenched with 5 mL of saturated NH_4Cl solution. This mixture was taken up in ether (70 mL) and washed with saturated NH_4Cl solution until the aqueous layer was colorless. The organic extract was washed with brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. Preparative TLC on silica gel using dichloromethane/ethyl acetate (10:1) as eluant gave 73.2 mg (42% yield) of 8 as a white solid: mp 120–124 °C; NMR ($CDCl_3$), Table I; IR ($CDCl_3$) 1730, 1690 cm^{-1}; mass spectrum, m/e 208 (M^+).

Synthesis of 10-Hydroxy-11,12-dioxatricyclo[5.3.1.1^{1,6}]dodeca-4,8-dien-3-one (10). To a cold (−78 °C) THF (9 mL) solution of dimer 5 (84.6 mg, 0.44 mmol) was added dropwise a solution of sodium aluminum bis(methoxyethoxy) dihydride in THF (1.65 mL, 0.133 M) under a nitrogen atmosphere. After the reaction mixture was warmed to 15 °C over 3 h, it was quenched with 5 mL of saturated NH_4Cl solution. A minimum amount of water was added to dissolve the resulting precipitate. This mixture was then extracted with ethyl acetate. The combined organic extracts were washed with saturated NH_4Cl solution, water, and brine and dried over anhydrous $MgSO_4$. Removal of the volatiles under reduced pressure afforded 74.1 mg of gummy solid. Preparative TLC on silica gel using dichloromethane/ethyl acetate (6:1) as eluant gave 11.2 mg (13% yield) of dimer 5 and 22.2 mg (26% yield) of keto alcohol 10: NMR (CD_3CN), Table I; IR ($CDCl_3$) 1690 cm^{-1}; mass spectrum, m/e 194 (M^+).

Registry No. 1 (R = Ac), 62644-49-9; 1 (R = H), 35436-57-8; 1 (R = $COCF_3$), 74036-55-8; 3, 74036-56-9; 5, 74036-57-0; 8, 74036-58-1; 10, 74036-59-2; lithium dimethylcuprate, 15681-48-8.

(9) O. Achmatowicy, Jr., P. Bukowski, B. Szechner, Z. Zwierzchowska, and A. Zamojski, *Tetrahedron*, 27, 1973 (1971).
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Base-Catalyzed Rearrangement of 4-Methyl-4-acetoxy-2,6-di-*tert*-butyl-2,5-cyclohexadienone

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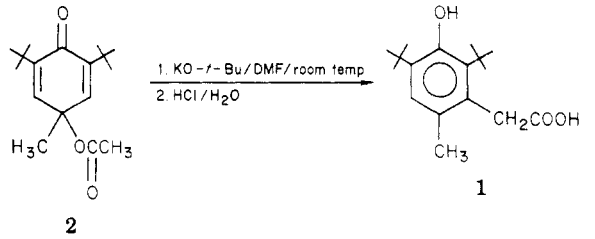
Recently, Nishinaga and co-workers[1] reported the synthesis of 1 by the rearrangement of 2 using potassium *tert*-butoxide (4:1 KO-*t*-Bu–2) in dimethylformamide, followed by acidification with aqueous hydrochloric acid. Compound 1 would be a very useful appendage in the synthesis of new antioxidants.[2] Our attempts to reproduce this work led to some interesting mechanistic observations.



2 1

When the rearrangement of 2 was carried out by using ≥2:1 potassium KO-*t*-Bu–2, 1 was isolated as reported.[1] However, when 1:1 KO-*t*-Bu–2 was used, there was isolated (50% yield) a white crystalline solid, mp 169–171 °C (CCl_4). (Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.24; H, 9.41), whose IR spectrum (KBr) exhibited absorptions at 1671 (α,β-unsaturated ketone) and 1762 cm^{-1} (five-membered lactone).[3] The ^1H NMR ($CDCl_3$) exhibited absorptions at 1.07 (s, 9 H), 1.17 (s, 9 H), 1.67 (s, 3 H), 6.12 (d, J = 2.0 Hz, 1 H), and 1.92–3.00 (m, 4 H) ppm downfield from internal Me_4Si. These values are clearly inconsistent with those values reported for 1 by Nishinaga and co-workers.[1]

The ^{13}C NMR spectrum was most revealing. Obtained under proton-decoupled conditions, 13 different carbon atoms were observed. However, under off-resonance conditions, seven of the carbon resonances exhibited cou-

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(2) Spivack, J. D.; Dexter, M. U.S. Patent 3 988 363, 1976.
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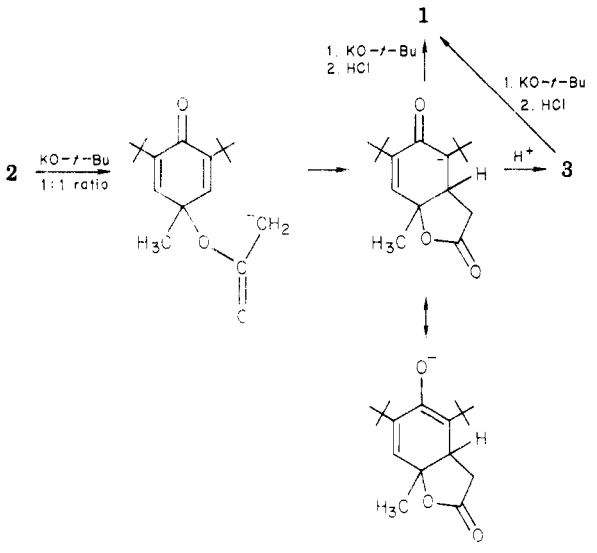
Table I. ^{13}C NMR Data for 3

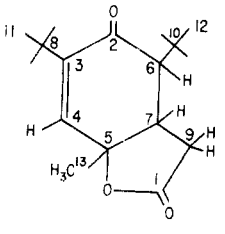
C atom	δ^a	mult[b]	C atom	δ^a	mult[b]
1	198.7	s	8	34.8	s
2	174.5	s	9	33.1	t
3	149.2	s	10	32.4	s
4	135.7	d	11	29.2	q
5	84.4	s	12	28.4	q
6	57.1	d	13	23.9	q
7	44.1	d			

[a] Downfield from ^{13}C signal of internal Me_4Si. [b] Off-resonance conditions.

Scheme I



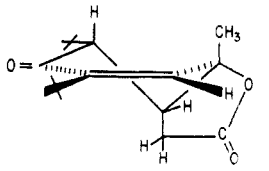
pling to attached protons. The ^{13}C NMR data, summarized in Table I, along with all the data above suggest structure **3**.



3

Clearly, **3** would be the expected intermediate in the rearrangement of **2** to **1**. Extraction by base of the acetoxy methyl proton of **2** and a subsequent Michael addition to the double bond, followed by protonation, would afford **3** (see Scheme I). However, all attempts to complete the rearrangement of **3** to **1** under acidic conditions (1, 6, or 12 M HCl in DMF, at 25 or 80 °C) led to unchanged **3**. When **3** was subjected to potassium *tert*-butoxide (≥1:1 ratio) under the original reaction conditions, followed by acidification with aqueous HCl, **1** was isolated in 95% yield. This suggests that a second equivalent of base is necessary to abstract the proton at C(7) of **3**, thus effecting elimination by either an E2 or E1cb mechanism, followed by aromatization.

The stereochemistry of **3** would then be important as to the ease by which an E2 elimination could occur. The ^1H NMR data show that the olefinic proton of **3** appears as a doublet (see above) indicating that it is long-range coupled to the proton at C(7). An examination of molecular models of **3** reveals that three different geometric configurations can exist at the ring fusions, assuming that the *tert*-butyl group exists in the equatorial position. However, only the geometry shown in **3a** places the two



3a

protons in a relationship approaching that of the "W" configuration,[4] thereby allowing for long-range coupling. The two leaving groups of **3a** are then in equatorial positions. However, there appears to be enough conformational flexibility at this end of the molecule to allow the leaving groups to become nearly diaxial during elimination without causing any substantial steric interactions in the remainder of the molecule.

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Registry No. **1**, 60901-78-2; **2**, 20778-60-3; **3**, 73908-05-1.

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Intramolecular Friedel-Crafts Acylation of a Lactone in Polyphosphoric Acid. Synthesis of 2-Phenylphenalen-1-one

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The tricyclic ring system of the antidepressant drug amitriptyline has inspired many endeavors toward molecular modifications.[1,2] During an SAR study of tetracyclic analogues, an attempt was made to synthesize 7*H*-benzo[5,6]cycloocta[1,2,3-*de*]naphthalen-7-one (**1**).[3] We report an intramolecular Friedel–Crafts acylation of 3-benzyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one (**2**) in polyphosphoric acid (PPA). The reaction did not lead to the desired ketone **1**, providing instead a convenient route to 2-phenylphenalen-1-one (**3**).

A Perkin condensation (under the Gabriel–Weiss modification[4]) of 1,8-naphthalic anhydride and phenylacetic acid gave a mixture of 2-phenylphenalen-1,3-dione and (*Z*)-3-phenylmethylene-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one (**4**).[5] The latter was separated and purified by column chromatography and recrystallization. Attempted reduction and hydrogenolysis of **4** with red phosphorous and boiling aqueous hydroiodic acid (57%) did not provide the expected 8-(2-phenylethyl)-1-naphthoic acid (**5**). Only reduction of the vinyl linkage occurred, giving **2** in 52%

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