tate gave 0.18 g of **14:** ^{1}H NMR ($CDCl_3$) δ 3.23 (s, 3 H, NCH_3), 4.81 (d, 1 H, vinyl, J = 3 Hz), 5.17 (d, 1 H, vinyl, J = 3 Hz), 7.4–7.9 (m, 4 H, aromatic); MS *m/e* 161 (M^+), 104, 78, 66; IR (neat) 1700 (C=O), 770, 700 cm^{-1}.

Hydrolysis of 7. A solution of **7** (1.77 g, 0.01 mol) in 0.1 N aqueous HCl (15 mL) on standing overnight deposited crystalline **3a** (1.5 g). A solution of **7** (0.88 g, 0.005 mol) in 6 N aqueous HCl (20 mL) was warmed to 80 °C, cooled, and extracted with chloroform (4 × 20 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure. The ^{1}H NMR and TLC characteristics of the concentrate (0.7 g) were qualitatively identical with those of the crude reaction mixture obtained on hydrolysis of **12:** Chromatography on silica gel eluting with ethyl acetate gave 0.15 g of **14.**

Acknowledgment. The authors wish to thank Dr. David Cochran for ^{13}C NMR spectra, Mr. Robert Rhodes for mass spectra, Mr. A. Augenblick for GLC analyses, Mr. K. B. Streeter and Mrs. Jan Stranick for the microanalyses, and Professor Gordon Gribble for many valuable discussions.

Registry No.—**3a,** 577-56-0; **3b,** 2360-45-4; **3c,** 19666-03-6; **3d,** 119-67-5; **4a,** 58083-35-5; **4b,** 58083-36-6; **4c,** 58083-39-9; **4d,** 58083-37-7; **4e,** 1726-16-5; **4f,** 66967-33-7; **4g,** 66967-34-8; **4h,** 5342-91-6; **4i,** 66967-35-9; **5,** 3453-64-3; **6,** 66967-36-0; **7,** 66967-29-1; **7** HCl, 66967-30-4; **12,** 29879-71-8; **13,** 66967-31-5; **13** HCl, 66967-32-6; **14,** 32360-90-0; methylamine, 74-89-5; sodium cyanoborohydride, 25895-60-7; ethylamine, 75-04-7; *n*-propylamine, 107-10-8; cyclopropylamine, 765-30-0; benzylamine, 100-46-9; 2-propylamine, 75-31-0.

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Fries Rearrangement of Trimethylhydroquinone Diacetate. A Novel Hydroquinone to Resorcinol Transformation

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Fries rearrangement of trimethylhydroquinone diacetate (**1b**) ($AlCl_3$, 220 °C) leads to 1-(2,6-dihydroxy-3,4,5-trimethylphenyl)ethanone (**4**) and not the expected (and previously reported) 1-(2,5-dihydroxy-3,4,6-trimethylphenyl)ethanone (**2a**). Resorcinol **4** arises via secondary rearrangements of the normal products **2a** and **2b.** A mechanistic rationale is proposed.

While pursuing synthetic studies aimed at (2*R*,4′*R*,8′*R*)-α-tocopherol (vitamin E),[1] we recently required dihydroxytrimethylacetophenone **2a** as a starting material. A search of the literature revealed two apparent preparations of this substance; however, the reported melting points were not in agreement. In 1938, von Werder and Jung[2] described **2a** as a yellow solid, mp 152 °C, prepared by Fries rearrangement of trimethylhydroquinone diacetate (**1b**) using aluminum chloride at 220 °C. On the other hand, Manecke and Bourwieg, in 1962, claimed that treatment of trimethylhydroquinone (**1a**) with boron trifluoride–acetic acid complex at 100 °C produced the monoacetate **2b** which, upon saponification, yielded **2a** obtained as a yellow solid, mp 111 °C. We have reinvestigated these transformations and now wish to report that while the latter material is, in fact, **2a,** the dihydroxyacetophenone isolated from high temperature aluminum chloride treatment of **1b** is the resorcinol **4.**

Results

Repetition of the boron trifluoride–acetic acid treatment of **1a**[3] smoothly gave **2b** which, in turn, yielded the acetyl hydroquinone **2a,** mp 107–108 °C, after exposure to methanolic sodium hydroxide. The spectral properties of this acetophenone as well as the derived diacetate **3** were in accord with the proposed structural arrangement (see below and Experimental Section).

In contrast, treatment of **1b** with aluminum chloride at 220 °C[2] led to a mixture of products which, although complex, was amenable to analysis by GC and GC–MS. While the major component was, in fact, a dihydroxytrimethylacetophenone (mol wt 194), its retention time was clearly different from that of **2a,** of which substance only trace amounts were detectable. In addition, two chromones were produced whose structures were subsequently proven to be **5a** and **5b** as proposed originally by von Werder and Jung.[2]

On a preparative scale, these three components could be isolated in quite pure form by column chromatography. The dihydroxyacetophenone so obtained was recrystallized several times yielding a yellow solid, mp 136–145 °C, which despite the broad melting range appeared homogeneous on GC analysis. For reasons that are not apparent, we were unable to obtain a sharp melting point for this substance through further recrystallization; nonetheless, we assume it is identical with the product for which von Werder and Jung reported mp 152 °C.

The ^{1}H NMR spectrum of this acetophenone was revealing in its relative simplicity (four singlets in a ratio of 2:3:3:6) which, in contrast to that of **2a** (six singlets in a ratio of 1:1:

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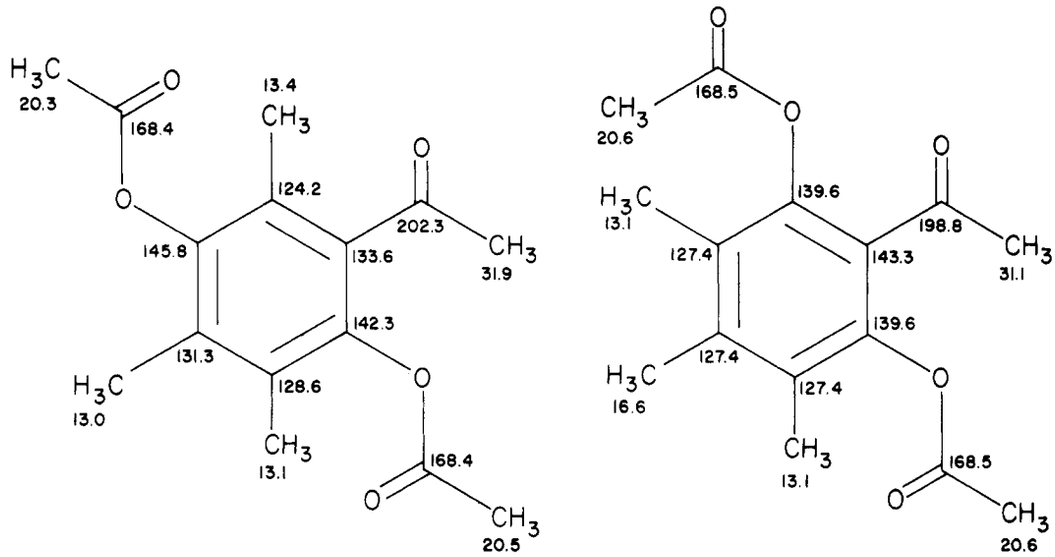
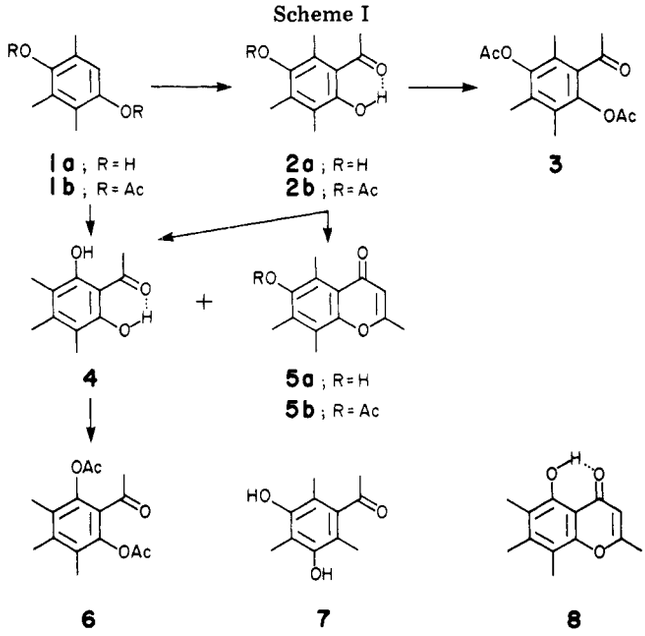


Figure 1. ^{13}C NMR of **3** and **6** taken from the wide-band ^1H-decoupled spectra measured in $CDCl_3$. Chemical shifts are in ppm relative to Me_4Si as an internal standard.

Scheme I



3:3:3:3), suggested the presence of a highly symmetrical structural arrangement. Of the six isomeric dihydroxytrimethylacetophenones, only two are symmetrical, namely **4** and **7**. However, the latter possibility was eliminated when it was noted that the observed product exhibited a carbonyl absorbtion at 1625 cm^{-1} compatible only with an H-bonded acetophenone. Furthermore, the ^1H NMR band due to the phenolic protons occurred at relatively low field (δ 10.45 ppm) again indicating the presence of intramolecular H bonding possible in **4**, but not in **7**. Final confirmation of structure **4** for the acetophenone derived from $AlCl_3$ rearrangement of **1b** was achieved by ^{13}C NMR spectroscopy. The proton decoupled ^{13}C NMR spectra of the derived diacetate **6** and the isomer **3** are summarized in Figure 1. Whereas **3** exhibits 14 distinct resonances, **6**, possessing mirror plane symmetry, gives rise to only nine, in agreement with the proposed structure.

Chromones **5a** and **5b** were prepared by independent synthesis for comparison purposes. Thus **2a** was treated with sodium hydride–ethyl acetate producing a β-diketone which was directly cyclized with HCl in acetic acid.[4,5] This gave **5b** (44%) which upon mild alkaline hydrolysis furnished the hydroxy chromone **5a.** These materials were identical with those produced in the $AlCl_3$ rearrangement of **1b.** Spectral examination (IR, NMR) of **5a** indicated the absence of intramolecular H bonding. In this manner it was established that the chromones derived from the Fries rearrangement originated from **2a** or **2b** and not from **4** in which case a 5-hydroxychromone (**8**) would have resulted.[6]

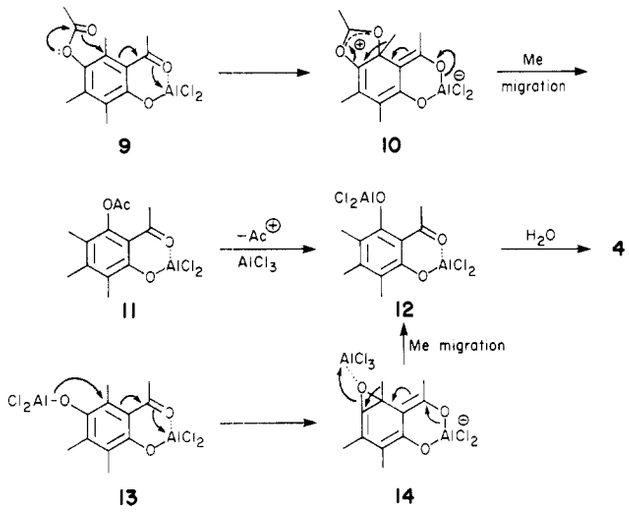
Further scrutiny of the Fries rearrangement ($AlCl_3$) of **1b** revealed that at temperatures below 220 °C (120–160 °C), mixtures containing both **2a** and **4** were obtained; the more vigorous the conditions, the more **4** was produced. In fact, we were unable to effect conversion of **1b** to **2a** or **2b** without the concomitant formation of substantial amounts of **4** using aluminum chloride. Since it appeared that **4** had arisen by further rearrangement of either **2a** or **2b,** we subjected both of the latter compounds to the reaction conditions. The results of these experiments as well as those involving **1b** are presented in Table I and clearly show that **4** is, in fact, derived from rearrangement of both **2a** and **2b.** The mixture obtained starting from **1b** and that from **2b** were similar in that **4, 5a,** and **5b** comprised 88% of the crude product. On the other hand, the mixture arising from **2a** was much more complex and contained a substantial amount (28%) of trimethylhydroquinone (**1a**) in addition to **4, 5a,** and **5b.** It should be noted that in all three experiments, several unidentified minor products were observed. One of these exhibited a molecular weight of 194 and is, therefore, assumed to be a third isomeric dihydroxytrimethylacetophenone. Because this substance was usually produced in very small quantities, its structure elucidation was not pursued.

Discussion

The migration of alkyl groups during the Fries rearrangement of phenolic esters with aluminum chloride is a well-known phenomenon.[7] In general, if the newly introduced acyl moiety encounters an ortho alkyl substituent, the alkyl group migrates to a meta position in order to relieve steric strain.[7b] The transformations of **2a** and **2b** to **4** represent additional examples of this type of rearrangement; however, the simultaneous 1,2 migration of an hydroxyl (or acetoxyl) group appears to be unprecedented and constitutes the rather remarkable conversion of a hydroquinone to a resorcinol.

A possible mechanistic rationale for this secondary rearrangement is delineated in Scheme II. Thus one might envi-

Scheme II



sion complex **9** (derived from **1b** via the initially formed **2b**) undergoing an intramolecular conjugate addition as shown, promoted by chelation with aluminum and leading to the zwitterionic enolate species **10.** Regeneration of the ketone moiety can then occur *with methyl migration* producing **11** in which the original *o*-methyl and *m*-acetoxyl substituents have been transposed. Deacetylation then yields complex **12** which on hydrolysis provides the observed resorcinol **4.** Alternatively, **12** could be derived from hydroquinone **2a** via intermediates **13** and **14** which are analogous to **9** and **10,** respectively. It should be noted, however, that the ring strain associated with epoxide **14** would render such an intermediate far less favorable than **10.** This may explain why the yield of **4** is substantially higher starting from **1b** or **2b** than from **2a** since, in the latter case, the relatively slow rate of formation of **14** could lead to the intervention of competitive reaction pathways such as the observed deacylation to give **1a.**

Two factors appear responsible for the propensity of hydroquinones **2a,b** to rearrange into resorcinol **4.** The first, and probably most significant, involves steric considerations. In complexes **9** and **13,** a severe steric interaction results from the proximity of the methyl substituent attached to the ketone moiety and that protruding from the ortho position of the aromatic ring (C-6). This unfavorable compression is relieved by the rearrangement to **12.** Secondly, the formation of **12** gives rise to a species having enhanced chelation ability by virtue of the 2,6-dihydroxy substitution pattern. With regard to the chromones **5a,b,** it should be recognized that the formation of these heterocycles like the deacetylation process (**2a** → **1a**) represents an alternative pathway by which the unfavorable steric interactions present in **9** and **13** can be alleviated.[8]

The failure to observe compounds **4, 5a,** or **5b** in the product derived from the boron trifluoride–acetic acid procedure[3] is probably due to the relatively mild conditions employed which, although sufficient to bring about the Fries rearrangement, are not capable of promoting the further rearrangements noted with neat aluminum chloride.

As a synthetic method for preparing resorcinols such as **4,** the aluminum chloride treatment of hydroquinone diacetates elucidated herein would appear to be severely limited in scope by the steric requirements mentioned above and, therefore, we have not pursued this line of investigation. However, we have encountered other examples of rather unusual chemistry associated with the congested nature of acetophenones **2a,b** and related compounds.[9] These studies will be reported in due course.

Table I. $AlCl_3$ Isomerizations[a]

starting material	registry no.	product distribution, %[b] 4[c,j]	5a[d,k]	5b[e,l]
1b	7479-28-9	62.9 (61.0[i])	8.4	16.8[f]
2a	64794-45-2	33.9 (28.9[i])	4.1	2.6[g]
2b	66901-79-9	54.6 (52.7[i])	14.1	19.2[h]

[a] 220 °C, 30 min. [b] Percentage of crude reaction product determined by GC analysis, Hewlett-Packard 5710A; 3 m × 4 mm (i.d.) column, 10% OV-101 on GCQ 100/120; temperature program for 80–260 °C, 2 °C/min; He carrier gas flow rate 30 mL/min. [c] Retention time 73 min; observed mol wt 194 (GC–MS). [d] Retention time 88 min; observed mol wt 218 (GC–MS). [e] Retention time 93 min; observed mol wt 260 (GC–MS). [f] Eight unidentified minor components present; **2a** (retention time 71 min) absent. [g] 27.6% **1a** present (retention time 56 min, observed mol wt 152 (GC–MS)) and 11 unidentified minor components; **2a** absent. [h] Six unidentified minor components present; **2a** absent. [i] Yield based on weight of crude product and percentage composition. [j] Registry no. 66842-24-8. [k] Registry no. 66842-25-9. [l] Registry no. 66842-26-0.

Experimental Section

All reactions were carried out under an atmosphere of argon. Melting points were determined in open capillaries and are uncorrected. The "usual work-up" involves dilution with water or saturated brine followed by three extractions with the specified solvent. The organic extracts were then combined, washed with saturated brine, dried over anhydrous magnesium sulfate, filtered, and concentrated at 40–50 °C under water aspirator pressure using a rotary evaporator. The residue was dried to constant weight under high vacuum. Column chromatography was performed using EM Silica Gel 60, 0.063–0.2 mm. Thin-layer chromatography was performed using EM 60F-254 precoated silica gel plates developed with either 1:1 hexane–ether or 1:1 toluene–ethyl acetate. Spots were detected with UV light and phosphomolybdic acid spray followed by heating. Infrared spectra were measured in chloroform solution and ultraviolet spectra in 95% ethanol. A Varian XL-100 instrument was used to obtain the NMR spectra. Chemical shifts are reported relative to tetramethylsilane as an internal standard. Low resolution mass spectral and GC–MS determinations were carried out using an electron energy of 70 V. Conditions for the GC separations are described in Table I.

1-(2,5-Dihydroxy-3,4,6-trimethylphenyl)ethanone (2a). Trimethylhydroquinone (**1a**) was converted into the monoacetate **2b** in 90% yield, using boron trifluoride–acetic acid complex as described previously.[3] Saponification of this material with methanolic sodium hydroxide gave **2a** in 71% yield, as a yellow solid, mp 107–108 °C (lit.[3] mp 111 °C), after recrystallization from carbon tetrachloride. In another experiment, a sample, mp 107–108.5 °C (from chloroform–hexane), exhibited: IR 3620 (OH), 1623 cm^{-1} (H-bonded C=O); UV_{max} 277 (ε 6650), 365 (2000), 215 (12 600) (sh), 240 nm (4600) (sh); NMR ($CDCl_3$) δ 11.59 (s, 1, bonded OH), 4.54 (s, 1, OH), 2.57 (s, 3, CH_3C=O), 2.39, 2.20, 2.15 (3s, 9, $ArCH_3$); NMR (Me_2SO-d_6) δ 8.53 (s, 1, bonded OH), 7.57 (s, 1, OH), 2.35 (s, 3, CH_3C=O), 2.04, 1.99, 1.96 (3s, 9, $ArCH_3$); MS, *m/e* 194 (M^+); TLC, R_f 0.26 (1:1 hexane–ether).

1-(2,5-Dihydroxy-3,4,6-trimethylphenyl)ethanone Diacetate (3). A solution of 0.2 g (1.03 mmol) of **2a** in 4 mL of pyridine and 3 mL of acetic anhydride was stirred at room temperature for 17 h then evaporated in vacuo. The residue was dissolved in dichloromethane and the solution was washed with saturated aqueous sodium bicarbonate then processed in the usual manner giving 0.28 g (96.1%) of **3** as a yellow solid. Recrystallization from ethanol afforded a tan solid: mp 116–118.5 °C (lit.[3] mp 123 °C); IR 1763 (ester C=O) 1698 cm^{-1} (ketone C=O); NMR ($CDCl_3$) δ 2.41 (s, 3, CH_3COAr), 2.32 (s, 3, CH_3CO_2Ar), 2.24 (s, 3, CH_3CO_2Ar), 2.07, 2.02 (2s, 9, $ArCH_3$); UV 210 (ε 16 700) (sh), 243 (3500) (sh), 280 nm (800) (sh); MS, *m/e* 278 (M^+).

Aluminum Chloride Rearrangements. a. Trimethylhydroquinone Diacetate (1b). An intimately ground mixture of 1.18 g (5 mmol) of trimethylhydroquinone diacetate (**1b**) and 1.76 g (13.1 mmol) of anhydrous aluminum chloride was heated at 220 °C for 30 min.[2] After cooling, the dark reaction mixture was treated with dilute aqueous hydrochloric acid and dichloromethane and the resulting mixture was stirred for 30 min at room temperature. Work-up with dichloromethane in the usual manner gave 0.94 g of a yellow-green solid (see Table I for GC analysis). This material was chromato-

graphed on 100 g of silica gel. Elution with 4:1 and 2:1 hexane–ether afforded 0.563 g of 1-(2,6-dihydroxy-3,4,5-trimethylphenyl)ethanone (**4**) (TLC, R_f 0.34, 1:1 hexane–ether) as a yellow solid, mp 124–140 °C, which was 86.6% pure by GC analysis (see Table I for conditions). Three crystallizations from ligroin (bp 60–90 °C) gave a yellow solid, mp 136–145 °C (lit.[2] mp 152 °C), which was 100% pure as determined by GC analysis: IR 3605 (OH), 1625 cm^{-1} (H-bonded C=O); UV_{max} 280 (14 900), 360 (2800), 210 (16 900) (sh), 224 nm (10 960) (sh) (lit.[2] UV_{max} 279, 360 nm); NMR (Me_2SO-d_6) δ 10.45 (s, 2, bonded **OH**), 2.70 (s, 3, CH_3C=O), 2.17 (s, 3, C-4 ArCH_3), 2.07 (s, 6, C-3, C-5 ArCH_3); MS, *m/e* 194 (M^+).

Further elution with pure ether gave 98 mg of acetoxy chromone **5b** as a tan solid (TLC, R_f 0.12), 93 mg of a mixture of chromones **5a** and **5b**, and 36 mg of hydroxychromone **5a** (R_f 0.07).

b. Dihydroxyacetophenone 2a. A 0.97-g (5 mmol) sample of **2a** was pyrolyzed with aluminum chloride (1.76 g) as described in part a. A 0.76-g portion of the crude brown solid product (0.827 g; GC analysis in Table I) was chromatographed on 100 g of silica gel. Elution with 2:1 hexane–ether gave 266 mg of a yellow-brown solid, mp 108–140 °C, composed mainly of resorcinol **4**. GC analysis revealed a purity of 78%.

c. Hydroxyacetoxyacetophenone 2b. A 1.18-g (5 mmol) sample of **2b** was pyrolyzed with aluminum chloride (1.76 g) as described in part a. The crude green solid product (0.937 g; GC analysis in Table I) was chromatographed on 100 g of silica gel. Elution with 4:1 and 2:1 hexane–ether gave 0.411 g of resorcinol **4** as a yellow solid, mp 126–136 °C, which was 91.5% pure as determined by GC analysis. Further elution with pure ether furnished 0.246 g of a solid mixture of chromones **5a** and **5b**.

1-(2,6-Dihydroxy-3,4,5-trimethylphenyl)ethanone Diacetate (6). A 0.1-g (0.52 mmol) sample of resorcinol **4** was acetylated as described above for the isomer **2a**. The crude product was recrystallized from ethanol giving 91 mg (63.6%) of diacetate **6** as a pale-yellow solid: mp 95–98 °C; IR 1765 (ester C=O), 1696 cm^{-1} (ketone C=O); UV_{max} 247 (ϵ 5650), 209 (19 200) (sh), 285 nm (1250) (sh); NMR ($CDCl_3$) δ 2.40 (s, 3, CH_3COAr), 2.26 (s, 6, Ar(OCOCH_3)$_2$), 2.24 (s, 3, ArCH_3), 2.06 (s, 6, Ar(CH_3)$_2$); MS, *m/e* 278 (M^+).

Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.94; H, 6.68.

6-Acetyloxy-2,5,7,8-tetramethyl-4*H*-1-benzopyran-4-one (5b). A 0.476-g (11.3 mmol) portion of 57% sodium hydride–oil dispersion was washed three times with hexane to remove the oil and then treated with ca. 10 drops of a solution of 0.5 g (2.58 mmol) of hydroquinone **2a** in 10 mL of dry ethyl acetate. An exothermic reaction began and the remainder of the solution was added dropwise with stirring, keeping the internal temperature below 30 °C. After stirring at room temperature for 20 min, the dark mixture was refluxed for 2 h then cooled and poured into 50 mL of ice–water containing 6 mL of glacial acetic acid. Work-up with ether in the usual manner gave a dark solid which was immediately treated with 15 mL of glacial acetic acid and 1 mL of concentrated hydrochloric acid. The mixture was refluxed for 30 min then cooled and concentrated under high vacuum. The residue was dissolved in dichloromethane and the solution was washed with saturated aqueous sodium bicarbonate solution then processed in the usual manner giving 0.5 g of a dark, solid residue. This material was chromatographed on 50 g of silica gel. Elution with 4:1 and 2:1 toluene–ethyl acetate afforded 300 mg (44.7%) of chromone **5b** as a tan solid, mp 162–171 °C. Recrystallization from ethanol yielded 230 mg (34.3%) of a colorless solid, mp 172–173.5 °C (lit.[2] mp 172 °C): IR 1760 (ester C=O), 1653 (chromone C=O), 1622 cm^{-1} (C=C); UV_{max} 228 (ϵ 24 600), 234 (24 750), 308 (6150), 246 (14 350) (sh), 252 (13 900) (sh), 265 (7900) (sh), 275 nm (5400) (sh); NMR ($CDCl_3$) δ 6.01 (s, 1, –C**H**=), 2.63 (s, 3, =C(O)CH_3), 2.36 (s, 3, OCOCH_3), 2.30, 2.31 (2s, 6, ArCH_3), 2.15 (s, 3, ArCH_3); MS, *m/e* 260 (M^+). This material was identical by TLC and NMR comparisons with the acetoxy chromone produced in the $AlCl_3$ rearrangements above.

6-Hydroxy-2,5,7,8-tetramethyl-4*H*-1-benzopyran-4-one (5a). A solution of 0.325 g (1.25 mmol) of acetoxy chromone **5b** prepared as in the preceding experiment and 0.345 g of potassium carbonate in 6 mL of methanol and 1 mL of water was stirred and refluxed for 1 h. The reaction mixture was cooled, diluted with water, and acidified with 1 N aqueous hydrochloric acid. The precipitated solid was filtered, washed with water, and dried giving 0.24 g (88%) of chromone **5a** as a colorless solid, mp 220–224 °C (lit.[2] mp 224 °C). Recrystallization from chloroform gave a colorless solid: mp 220–222 °C; IR 3620 (OH), 1652 (ketone C=O), 1620 cm^{-1} (C=C); UV_{max} 206 (ϵ 22 650), 238 (18 100), 330 (5480), 253 nm (14 650) (sh); NMR ($CDCl_3$) δ 6.03 (s, 1, =C**H**–), 5.04 (br s, 1, **OH**), 2.77 (s, 3, =C(O)CH_3), 2.34, 2.31 (2s, 9, ArCH_3); MS, *m/e* 218 (M^+).

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Registry No.—**3**, 66842-27-1; **6**, 66842-28-2.

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(5) von Werder and Jung[2] also reported an independent synthesis of **5a** involving condensation of **1a** with ethyl acetoacetate in the presence of phosphorus pentoxide, at 140 °C. However, because of the low yield reported and rather brutal conditions employed, we chose the alternative procedure described herein in order to facilitate the isolation of pure samples of chromones **5a,b** for spectral analysis.
(6) See G. P. Ellis, Ed., "Chemistry of Heterocyclic Compounds. Chromenes, Chromanones, and Chromones", Wiley, New York, N.Y., 1977, Chapter XII.
(7) Cf. (a) R. Martin, *Bull. Soc. Chim. Fr.*, 1519 (1974); (b) K. v. Auwers, H. Bundesmann, and F. Wieners, *Justus Liebigs Ann. Chem.*, **447**, 162 (1926); (c) J. N. Chatterjea, S. N. P. Gupta, and V. N. Mehrotra, *J. Indian Chem. Soc.*, **42**, 205 (1965).
(8) It is interesting to note that treatment of 2,4-dichloro-5-methylphenyl acetate with aluminum chloride at 135 °C produces 6,8-dichloro-2,5-dimethylchromone and 2,4-dichloro-5-methylphenol in addition to the major and expected Fries rearrangement product 3,5-dichloro-2-hydroxy-6-methylacetophenone: S. E. Cremer and D. S. Tarbell, *J. Org. Chem.*, **26**, 3653 (1961).
(9) Unpublished observations of N. Cohen, R. J. Lopresti, and D. Trullinger.