1,1-difluoro-2-(*m*-trifluoromethylphenyl)ethane, 50562-17-9; *p*-fluoro-α,α,α-trifluoroacetophenone, 655-32-3; 1-phenyl-2,2,2-trifluoroethanol, 340-04-5; 1-(*m*-tolyl)-2,2,2-trifluoroethanol tosylate, 655-32-3; 1-(*p*-fluorophenyl)-2,2,2-trifluoroethanol, 50562-19-1, 50562-20-4 (tosylate); 1-(*m*-trifluoromethylphenyl)-2,2,2-trifluoroethanol tosylate, 50562-21-5; 1,1,1-trifluoro-2-(*m*-trifluoromethylphenyl)ethane, 50562-22-6; 2,2-difluoro-1-phenylethanol-*1*-d_1, 50562-23-7, 50562-24-8 (tosylate).

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Steric and Electronic Factors Which Effect the Thermal Cyclization of Meta-Substituted Aryl Propargyl Ethers. Synthesis of 5- and 7-Substituted 3-Chromenes[1]

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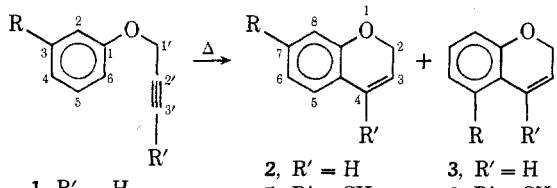
The thermal cyclization of meta-substituted phenyl propargyl ethers (**1** and **4**) proceeded to yield a mixture of 5- and 7-substituted 3-chromenes. The ratio of chromene isomers was somewhat dependent upon the nature of the starting materials. Thus, terminal acetylenes (**1**) gave a mixture of **2** and **3** (resulting from para and ortho cyclization, respectively) with the latter product usually in slight excess. Nonterminal acetylenes (**4**) also gave a mixture of ortho- and para-cyclized products (**6** and **5**, respectively); however, para cyclization was found to be favored. Regioselective cyclization was greatest for **4d**, which gave a mixture of 4,7- and 4,5-dimethyl-3-chromene in a ratio of 2:1. The cyclization of 3-(3-methoxyphenyloxy)-3-methylbutyne (**16**) also proceeded with little regioselectivity to give a mixture of **17** and **18**. The effects of electron-donating and electron-withdrawing meta substituents were also studied.

In our initial studies[2] on the thermal cyclization of aryl propargyl ethers we found that the cyclization of **1a** did not proceed in the regioselective manner previously reported.[3] Instead, the cyclization of **1a** led to the formation of both **2a** and **3a** where, in fact, the previously unreported 5-methoxy isomer (**3a**) was the more abundant product. Our interest in the use of certain substituted chromenes as intermediates in the synthesis of tumor-inhibitory trichothecan mycotoxins[4] prompted us to further examine those factors which influence regioselectivity in this reaction and to study the effects of various substituents on the aromatic ring.



1, R′ = H
4, R′ = CH_3

2, R′ = H
5, R′ = CH_3

3, R′ = H
6, R′ = CH_3

a, R = OCH_3
b, R = $COCH_3$
c, R = $N(C_2H_5)_2$
d, R = CH_3
e, R = $OCOCH_3$

The aryl propargyl ethers used in this study were synthesized by a Williamson reaction using the appropriately substituted phenols and propargyl bromides.[2] The cyclization of the aryl propargyl ethers was carried out in *N,N*-diethylaniline at 210–215°;[2] the isolated yield of the cyclized products, boiling points, reaction times, and product ratios are given in Table I.

The structures of the various chromene isomers were determined by comparison of nmr spectra. Typical 1,2,3- and 1,2,4-trisubstituted benzene patterns were generally evident in the nmr spectra of the 5 and 7 isomers ($J_o \cong 8$ and $J_m \cong 2$ Hz).

In the nmr spectra of the various chromenes the C-2 protons always appeared at slightly higher field in the 5-substituted isomer compared to the 7-substituted isomer. Similarly, the C-3 proton appeared at slightly lower field in the 5 isomer compared to the 7 isomer. The C-4 proton (or the C-4′ methyl protons) generally appeared at lower field in the nmr spectra of the 5-substituted compound compared to the 7 isomer. One exception to this latter

Table I
Thermal Cyclization of Meta-Substituted Aryl Propargyl Ethers (1 or 4)

Compd	R	Reaction time, hr	Yield, %	Bp, °C (mm)	Ortho:para[a] ratio
1a[2]	OCH_3	18.5	51	54 (0.6)	54:46
4a	OCH_3	30	86	93.5 (0.4)	47:53
1b[b]	$COCH_3$	15	<10		
4b	$COCH_3$	48	75	113–114 (0.4)	55:45
1c	$N(C_2H_5)_2$	15	<20	109 (1.5)	100:<1
4c[b]	$N(C_2H_5)_2$	30	<3		
1d	CH_3	15	89[c]	66 (0.45)	47:53
4d	CH_3	48	92[d]	88–90 (2.1)	36:64
1e	$OCOCH_3$	15	51	102 (0.45)	57:43
4e	$OCOCH_3$	48	96[d]	129 (2.3)	47:54

[a] Ortho cyclization affords the 5-substituted chromene (**3** or **6**) and para cyclization affords the 7-substituted chromene (**2** or **5**). Ortho:para ratios were determined by glc. [b] Insufficient quantities of the product(s) did not permit accurate determination of boiling point and isomer ratios. [c] The cyclization of 3-(*p*-methylphenyloxy)propyne (**19**) afforded only a 67% yield of 6-methyl-3-chromene [**20**, bp 73–74° (1.6 mm); 15 hr reaction time]. [d] These yields were calculated on the basis of *ca.* 20% recovery of starting material.

Table II
Europium-Induced Shifts in the Nmr Spectra (CCl_4, TMS) of 5- and 7-Aceto-4-methyl-3-chromene (6b and 5b)

Compd	Downfield shift, Hz C-2	C-3	C-4′	CH_3CO
5b	18	10	13	129
6b	35	35	101	163

generalization was noted in the case of **5b** and **6b**; in the case of **6b** the ketone carbonyl shielded the C-4′ methyl protons, causing them to appear at higher field than the corresponding methyl protons in the 7 isomer (**5b**).

The nmr spectra of **5b** and **6b** were recorded with added Euroshift-F and the shifts are reported in Table II. The magnitude of the shift for the methyl ketone signal, compared to that for the C-2 and C-3 protons, clearly indicates that the europium formed a complex with the ketone moiety and not the ring oxygen. The magnitude of the shift for the C-4′ methyl protons in **6a** compared to **5a** clearly establishes the structures of the two isomers. The europium-induced shifts in the aromatic region of the spectra of **5b** and **6b** also permitted unambiguous interpretation of the aromatic substitution pattern which was confirmed by spin–spin decoupling experiments.

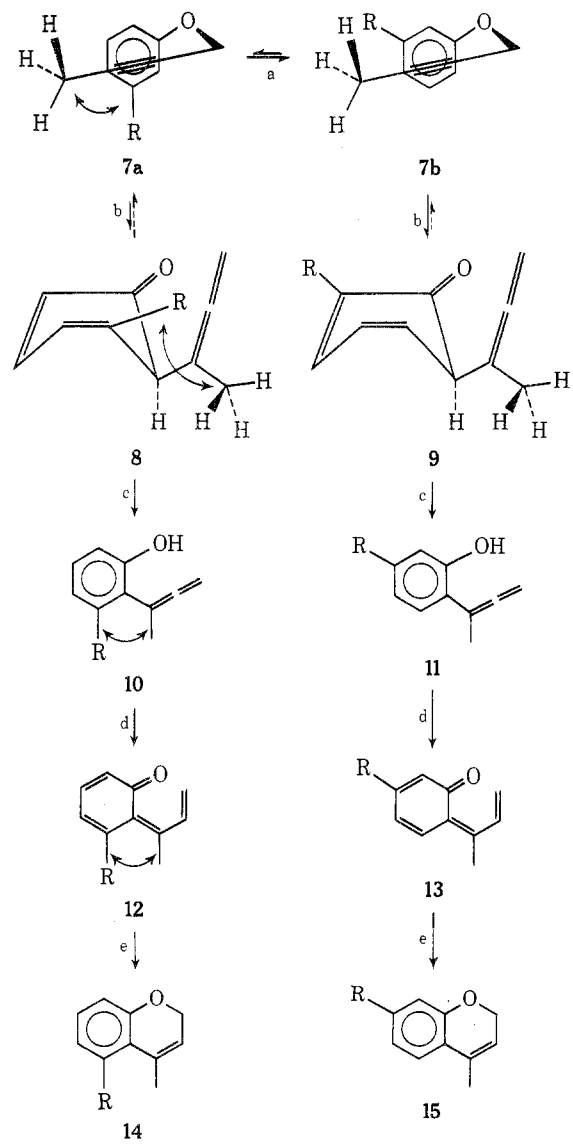
Support for the nmr structural assignments was obtained from a comparison of the ir spectra of the 5- and 7-substituted isomers in the out-of-plane bending region below *ca.* 900 cm^{-1}.

It is evident, from examination of the data presented in Table I, that the incorporation of a 3′-methyl substituent in the aryl propargyl ether usually resulted in an increased tendancy for the cyclization to occur para to the 3 substituent on the aromatic ring (*cf.* para:ortho ratios in the cyclization of **4** relative to **1**).

In the thermal cyclization of aryl propargyl ethers (*e.g.*, **7**) the obvious determinant of regioselectivity is the initial Claisen rearrangement (reaction b, Scheme I). It is difficult, however, to propose a specific rationalization for the regioselectivity, since the product-determining step in the mechanistic sequence[5] is not known.

The initial [3,3] sigmatropic rearrangement can occur either ortho or para to the 3 substituent on the aromatic ring. In the rearrangement of **7** to **8** (*i.e.*, cyclization ortho to the aryl substituent) the aryl propargyl ether must assume a conformation like **7a**; in this conformation there is a steric interaction between the C-3 substituent and the C-4′ methyl group which could increase the energy requirement in the conversion of **7a** to **8**. In the rearrangement to **9** the conformation necessary for this reaction, **7b**, is not sterically encumbered.

Scheme I



The steric interaction between the C-4′ methyl group and the C-3 substituent may become more severe in the transition state leading to **8**. As C-2 and C-3′ rehybridize the substituents on these two carbon atoms move closer together. While the exact geometry of the transition state is uncertain, this latter interaction is evident from the structure of the allene intermediate (**8**) wherein these two substituents lie in somewhat closer proximity relative to

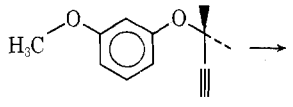
7a. Once again a similar steric interaction does not exist in the rearrangement of 7b to 9.

The observation (Table I) that the highest degree of regioselectivity was attained in the cyclization of 4d would support this hypothesis, since the tetravalent carbon would be expected to offer the greatest degree of steric hindrance in the series examined.

The next step in the mechanistic sequence is the enolization of the dienone (8 or 9). Normally the enolization process is considered to be rapid; however, in the case of the Claisen rearrangement of meta-substituted allyl phenyl ethers steric hindrance has been suggested as a factor which may retard this process.[6] Thus if the rearrangement of 7a to 8 is reversible then the steric hindrance of enolization of 8 would tend to drive the reaction through 9 to yield the 7-substituted 3-chromene (15).

It would appear unlikely that the phenolic allene intermediate (10 or 11) would revert back to the dienone; thus any observed regioselectivity must be a consequence of one or both of the first two steps.

Recently the cyclization of the meta-substituted aryl α,α-dimethylpropargyl ether 16 was reported to proceed in a regioselective fashion to yield 17.[7] Based upon our experience with this reaction the regioselectivity appeared unlikely. In our hands the cyclization of 16 afforded a mixture of 17 and 18 in approximately equal amounts. The nmr spectrum of the mixture of 17 and 18 very clearly showed the presence of the two isomers and the structures were confirmed by nmr and ir following glc separation. The discrepancy between our results and those of Hlubucek, *et al.*,[7] is difficult to rationalize, particularly since the latter workers did report the nmr spectrum of 17. Furthermore, these workers did examine the crude reaction product (glc and nmr) and concluded that if 18 was formed it was present to the extent of less than 3%.[7]



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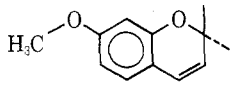
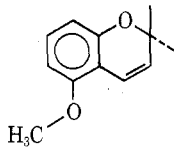


17



18

More recently it has been reported that 2-hydroxy-4-(1′,1′-dimethylprop-2-ynyloxy)acetophenone undergoes regioselective ortho cyclization. 2-Acetoxy-4-(1′,1′-dimethylprop-2-ynyloxy)acetophenone, on the other hand, cyclized to give a 1:2 ratio of para- and ortho-cyclized products.[8]

Iwai and Ide, on the basis of a few examples, concluded that resonance electron-donating substituents in the meta position (*i.e.*, ortho or para to the aromatic terminus in the Claisen rearrangement) facilitated the cyclization of the aryl propargyl ethers to the corresponding 3-chromenes (*i.e.*, higher product yield).[3] In our study we chose a range of electron-withdrawing ($OCOCH_3$ and $COCH_3$) and electron-donating (CH_3, OCH_3, and NEt_2) substituents to study the electronic effects (on the yield in this reaction).

Based upon the data given in Table I and on previous observations[2,5c] it is obvious that electronic effects do have a significant influence upon the reaction.

In the cyclization of 1 both strongly electron-donating and electron-withdrawing substituents appear to have an adverse effect upon the reaction. In the cyclization of both 1b and 1c the yield of chromenes was low and the reaction was accompanied by extensive polymerization. In the cyclization of 4 the reaction proceeded reasonably well with a strong electron-withdrawing substituent (*cf.* 4b); however, it gave little or no cyclized product in the case of a strong electron-donating substituent (*cf.* 4c).

A comparison of 4a, 4d, and 4e revealed that the yields increased as the electron-donating properties of the meta substituent decreased. Furthermore, based on reaction times and recovery of starting material, the reactions appeared to proceed faster with electron-donating meta substituents.

The data are most readily explained with the assumption that the initial Claisen rearrangement is the rate-limiting step[5a] in the reaction sequence. Electron-withdrawing meta substituents will decrease the electron density at the aromatic terminus of the Claisen rearrangement and retard the reaction. Thus, in the case of a strong electron-withdrawing substituent the rate of the Claisen rearrangement is sufficiently slow so as to permit polymerization of the terminal acetylene to become a major side reaction. This would explain the marked increase in yield that was observed in the cyclization of the nonterminal acetylene, 4b, compared to the terminal acetylene, 1b.

Electron-donating meta substituents would increase the rate of the initial Claisen rearrangement and retard the enolization of the allenic dienone intermediates, 8 and 9. Strong electron-donating substituents could retard the enolization to the extent that side reactions with 8 and 9 become dominant.[9] This effect along with a possible steric hindrance of enolization could explain why the cyclization of 4c proceeded so poorly.

Further research will be directed toward a study of solvent effects on the regioselectivity of this cyclization reaction. It is possible that contaminants (*e.g.*, mono-*N*-ethylaniline or trace metals) may exert an influence which could explain the difference between our data and those previously reported for the cyclization of 16.[7]

Table III
Preparation of the Aryl Propargyl Ether Intermediates

Compd[a]	R	R′	Bp, °C (mm)	Yield, %
1a	H	OCH_3	109.5 (4.5)	84
4a	CH_3	OCH_3	96 (0.6)	85
1b	H	$COCH_3$	99 (0.32)	86
4b	CH_3	$COCH_3$	114 (0.9)	79
1c	H	$N(C_2H_5)_2$	118 (0.4)	31
4c	CH_3	$N(C_2H_5)_2$	159 (3.0)	56
1d	H	CH_3	75 (1.5)	95
4d	CH_3	CH_3	90 (2.1)	80
1e	H	$OCOCH_3$	114 (0.7)	69
4e	CH_3	$OCOCH_3$	113–114 (0.5)	55
19	H	*p*-CH_3	69 (1.4)	79

[a] Satisfactory microanalytical data (±0.3% for C, H, and N) were reported for all compounds listed.

Experimental Section

Nmr spectra were determined in CCl_4 solution (containing *ca.* 1% TMS as an internal standard) on a Varian T-60 spectrometer; peak positions of multiple signals were confirmed by spin-spin decoupling. Infrared spectra were determined neat using a Perkin-Elmer Model 237 spectrophotometer. The uv spectra were determined in 95% ethanol solution on a Beckman DB-G grating spectrophotometer. The purity of analytical and spectral samples was confirmed by glc and ortho:para ratios were determined by photocopying the chromatogram, cutting out the chromatographic peak, and weighing the paper (Varian Aerograph Model 90-P with a thermal conductivity detector); nitrogen was used as the carrier gas and gas flow rates were *ca.* 176 ml/min except for that of 5d and 6d, which was *ca.* 52 ml/min. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The aryl propargyl ethers were prepared according to the method previously described.[2] The yields and boiling points of the aryl propargyl ethers are given in Table III.

The 3-chromenes were prepared according to the method previously described[2] and reaction times, per cent yields, boiling points, and isomer ratios are given in Table I. Satisfactory microanalytical data (±0.4% for C, H, and N) were reported for all new compounds prepared.

5-Methoxy- and 7-Methoxy-4-methyl-3-chromene (6a and 5a). The isomeric mixture was separated by preparative glc (30% Carbowax, 12 ft × 0.375 in. column at 240° with 50-μl injection) to yield **6a** and **5a** with retention times of 21.4 and 27.5 min, respectively. **6a** had ir 938 (w), 909 (w), 780 (m), 763 (m), and 733 cm^{-1} (w); uv max 228 nm (ε 9330) and 276 (4650); nmr δ 2.14 (q, 3, $J_{4',3} \cong J_{4',2}$ = 1.6 Hz), 3.77 (s, 3), 4.53 (pair of q, 2, $J_{2,3}$ = 4.5 Hz), 5.44–5.64 (m, 1), 6.34–6.75 (m, 2), and 7.05 (t, 1, J_o = 8 Hz). **5a**[10] had ir 998 (w), 839 (w), 807 (m), and 745 cm^{-1} (w); uv max 228 nm (ε 16,400), 272 (3890), and 312 (1600); nmr δ 1.97 (q, 3, $J_{4',3} \cong J_{4',2}$ = 1.6 Hz), 3.72 (s, 3), 4.75 (pair of q, 2, $J_{2,3}$ = 4.0 Hz), 5.32–5.52 (m, 1), 6.32–6.53 (m, 2), and 6.91–7.13 (pair of t, 1).

5-Aceto- and 7-Aceto-4-methyl-3-chromene (6b and 5b). The isomeric mixture was separated by preparative glc (30% Carbowax, 12 ft × 0.375 in. column at 220° with 100-μl injections) to yield **6b** and **5b** with retention times of 78 and 147.6 min, respectively. **6b** had ir 1686 (s), 922 (w), 876 (m), 790 (s), 770 (w), 747(m), and 710 cm^{-1} (w); uv max 223 nm (ε 10,800), 262 (6310), and 328 (2940); nmr δ 1.87 (q, 3, $J_{4',3} \cong J_{4',2}$ = 1.5 Hz), 2.50 (s, 3), 4.58 (pair of q, 2, $J_{2,3}$ = 4.4 Hz), 5.65–5.89 (m, 1), and 6.85–7.40 m, 3). **5b** had ir 1678 (s), 958 (w), 918 (w), 884 (m), 835 (s), and 749 cm^{-1} (w); uv max 237 nm (ε 12,700), 291 (6480), and 340 (3650); nmr δ 2.02 (q, 3, $J_{4',3} \cong J_{4',2}$ = 1.9 Hz), 2.46 (s, 3), 4.38 (pair of q, 2, $J_{2,3}$ = 3.7, $J_{2,4'}$ = 1.9 Hz), 5.57–5.83 (m, 1), and 7.07–7.60 (m, 3).

5-(*N,N*-Diethylamino)-3-chromene (3c) was purified by preparative glc (20% SE-30, 5 ft × 0.375 in. column at 220° with 25-μl injections) with a retention time of 9.4 min: ir 1018 (m), 977 (w), 766 (s), and 750 cm^{-1} (s); uv max 218 nm (ε 15,100), 225 (9490), and 292 (5730); nmr δ 1.0 (t, 6, J = 7 Hz), 3.02 (q, 4), 4.70 (pair of d, $J_{2,3}$ = 4, $J_{2,4}$ = 1.9 Hz), 5.72 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.48–6.68 (m, 4), and 7.09 (t, 1, J_o = 8 Hz).

7-Methyl- and 5-Methyl-3-chromene (2d and 3d). The isomeric mixture was separated by preparative glc (30% Carbowax, 12 ft × 0.375 in. column at 180° with 50-μl injection) to yield **2d** and **3d** with retention times of 40.3 and 45.8 min, respectively. **2d** had ir 1035 (s), 1021 (w), 945 (w), 812 (s), 742 (w), and 679 cm^{-1} (w); uv max 226 nm (ε 14,600), 271 (4230), and 310 (3160); nmr δ 2.27 (s, 3), 4.83 (q, 2, $J_{2,3}$ = 3.5, $J_{2,4}$ = 1.9 Hz), 5.70 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.43 (pair of t, 1), and 6.55–6.95 (m, 3). **3d** had ir 1020 (m), 951 (w), 772 (s), 753 (s), 678 (w), and 653 cm^{-1} (w); uv max 228 nm (ε 10,700), 272 (4470), and 310 (2080); nmr δ 2.25 (s, 3), 4.76 (q, 2, $J_{2,3}$ = 3.8, $J_{2,4}$ = 1.9 Hz), 5.81 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.66 (pair of t, 1), 6.49–6.80 (m, 2), and 7.00 (t, 1, J_o = 7.7 Hz).

7-Methyl- and 5-Methyl-4-methyl-3-chromene (5d and 6d). The isomeric mixture was separated by preparative glc (30% Carbowax, 12 ft × 0.375 in. column at 220° with 10-μl injections) to yield **5d** and **6d** with retention times of 127.2 and 139.8 min, respectively. **5d** had ir 1020 (m), 936 (w), 814 (s), and 784 cm^{-1} (w); uv max 221 nm (ε 13,200), 260 (3820), and 307 (2530); nmr δ 1.96 (q, 3, $J_{4',2} \cong J_{4',3}$ = 1.8 Hz), 2.26 (s, 3), 4.75 (pair of q, $J_{2,3}$ = 4.0, $J_{2,4'}$ = 1.8 Hz), 5.46–5.66 (m, 1), and 6.54–7.13 (m, 3). **6d**[10] had ir 1015 (m), 937 (m), 911 (w), 784 (s), 771 (s), 741 (m), and 708 cm^{-1} (w); uv max 223 nm (ε 17,200), 263 (5910), and 305 (2650); nmr δ 2.17 (q, 3, $J_{4',2} \cong J_{4',3}$ = 1.6 Hz), 2.44 (s, 3), 4.43 (pair of q, $J_{2,3}$ = 4.5 Hz), 5.56–5.91 (m, 1), and 6.56–7.24 (m, 3).

5-Acetoxy- and 7-Acetoxy-3-chromene (3e and 2e). The isomeric mixture was separated by preparative glc (30% NPGA, 12 ft × 0.375 in. column at 180° with 50-μl injections) to yield **3e** and **2e** with retention times of 76.4 and 88.6 min, respectively. **3e** had ir 1770 (s), 982 (m), 921 (m), 793 (w), 772 (m), and 749 cm^{-1} (s); uv max 228 nm (ε 16,400), 272 (3890), and 312 (1596); nmr δ 2.23 (s, 3), 4.82 (q, 2, $J_{2,3}$ = 3.5, $J_{2,4}$ = 1.9 Hz), 5.77 (pair of t, 1, $J_{3,4}$ = 10 Hz), 6.44 (pair of t, 1), 6.50–6.75 (m, 2), and 7.09 (t, 1, J = 8 Hz). **2e** had ir 1767 (s), 1034 (m), 1007 (w), 783 (m), and 753 cm^{-1} (s); uv max 229 nm (ε 10,500), 275 (3370), and 311 nm (3320); nmr δ 2.20 (s, 3), 4.90 (q, 2, $J_{2,3}$ = 3.5, $J_{2,4}$ = 1.6 Hz), 5.76 (pair of t, 1, $J_{3,4}$ = 10 Hz), 6.46 (pair of t, 1), 6.46–6.64 (m, 2), and 6.82–7.05 (m, 1).

5-Acetoxy- and 7-Acetoxy-4-methyl-3-chromene (6e and 5e). The isomeric mixture was separated by preparative glc (30% SE-30, 20 ft × 0.375 in. column at 230° with 50-μl injections) to yield **6e** and **5e** with retention times of 41.6 and 50.0 min, respectively. **6e** had ir 1764 (s), 970 (m), 916 (w), 865 (w), 789 (m), 769 (m), 738 (w), and 698 cm^{-1} (w); uv max 225 nm (ε 10,400), 267 (3240), and 307 (2960); nmr δ 2.07 (q, 3, $J_{4',2} \cong J_{4',3}$ = 1.5 Hz), 2.20 (s, 3), 4.62 (pair of q, 2, $_{2,3}$ = 4 Hz), 5.48–5.68 (m, 1), 6.56 (pair of d, 1, J_o = 10, J_m = 1.4 Hz), 6.72 (pair of d, 1), and 7.13 (t, 1). **5e** had ir 1767 (s), 1015 (m), 950 (w), 907 (m), 897 (m), 819 (m), 787 (w), and 761 cm^{-1} (w); uv max 220 nm (ε 8730), 267 (2540), and 306 (3140); nmr δ 2.00 (q, 3, $J_{4',3} \cong _{4',2}$ = 1.6 Hz), 2.22 (s, 3), 4.83 (pair of q, 2, $J_{2,3}$ = 3.5 Hz), 5.46–5.66 (m, 1), 6.50–6.89 (m, 2), and 6.93–7.30 (m, 1).

7-Methoxy- and 5-Methoxy-2,2-dimethyl-3-chromene (17 and 18). 3-(3-Methoxyphenyloxy)-3-methylbutyne (16)[7] was cyclized in *N,N*-diethylaniline heated under reflux according to the method of Hlubucek, *et al.*[7] In two additonal experiments **16** was cyclized in a *N,N*-diethylaniline solution heated on an oil bath at 210–215° for 8 hr under a nitrogen atmosphere. In all three experiments the results were substantially the same [*ca.* 85% yield, bp 104–105° (1.4 mm)].

The isomeric mixture was separated by preparative glc (30% Carbowax, 12 ft × 0.375 in. column at 220° with 100–200 μl injections) to yield **17** and **18** with retention times of 28.9 and 23.6 min, respectively, in a ratio of 49:51. **17** had ir 1031 (m), 998 (m), 831 (w), 799 (w), and 702 cm^{-1} (w); uv max 222 nm (ε 19,800), 281 (6970), and 304 (6270); nmr δ 1.40 (s, 6), 3.75 (s, 3), 5.41 (d, 1, $J_{3,4}$ = 10 Hz), 6.23 (d, 1, $J_{3,4}$ = 10 Hz), 6.43 (m, 2), and 6.84 (d, 1, J_o = 9 Hz). **18** had ir 989 (w), 888 (m), 791 (w), and 750 cm^{-1} (s); uv max 226 nm (ε 18,100) and 278 (7260); nmr δ 1.40 (s, 6), 3.80 (s, 3) 5.48 (d, 1, $J_{3,4}$ = 10 Hz), 6.32 (d of d, 2, J_o = 8, J_m = 2.5 Hz), 6.63 (d, 1), and 6.99 (t, 1, J_o = 8 Hz).

6-Methyl-3-chromene (20)[11] had ir 1038 (s), 1031 (m), 936 (w), 920 (w), 874 (w), 816 (s), 760 (m), 753 (m), 705 (w), and 680 cm^{-1} (w); uv max 223 nm (ε 19,600), 265 (4010), and 314 (3000); nmr δ 2.21 (s, 3), 4.77 (q, 2, $J_{2,3}$ = 3.4, $J_{2,4}$ = 1.9 Hz), 5.72 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.39 (pair of t, 1), and 6.52–7.06 (m, 3).

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Registry No.—**1a,** 41580-72-7; **1b,** 34264-13-6; **1c,** 50584-90-2; **1d,** 5651-89-8; **1e,** 50584-91-3; **2a,** 18385-89-2; **2d,** 18385-88-1; **2e,** 50584-92-4; **3a,** 41580-69-2; **3c,** 50584-93-5; **3d,** 50584-94-6; **3e,** 13849-33-7; **4a,** 50584-95-7; **4b,** 50584-96-8; **4c,** 50584-97-9; **4d,** 50584-98-0; **4e,** 50584-99-1; **5a,** 50585-00-7; **5b,** 50585-01-8; **5d,** 50585-02-9; **5e,** 50585-03-0; **6a,** 50585-04-1; **6b,** 50585-05-2; **6d,** 50585-06-3; **6e,** 50585-07-4; **16,** 34191-90-7; **17,** 17598-02-6; **18,** 13162-78-2; **19,** 5651-90-1; **20,** 18385-83-6.

References and Notes

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