Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.27; H, 10.81.

Tricyclo[6.2.1.0^{4,11}]undecan-2-ol was obtained from **22** in 89% yield according to the above procedure: mp 97.1–98°; ir (CCl_4) 3590 and 3430 cm^{-1}; nmr ($CDCl_3$) δ 4.32 (m, 1, –CHOH) and 1.72 (br s, 1, –OH); mass spectrum (70 eV) no M^+, *m/e* 148 results from loss of H_2O from parent.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.71; H, 10.69.

Tricyclo[7.2.1.0^{5,12}]dodecan-10-ol was obtained as an oil in quantitative yield from tricyclo[7.2.1.0^{5,12}]dodecan-10-one by the above procedure: bp (bath temperature) 80° (0.3 mm); ir (CCl_4) 3590 and 3350 cm^{-1}; nmr (CCl_4) δ 3.70 (m, 1, –CHOH) and 2.90 (br s, 1, –OH); glpc (10% Carbowax 1000, 6 ft × 0.125 in., 160°, 50 ml/min He) shows a single peak; mass spectrum (70 eV) *m/e* 180 (M^+).

Anal. Calcd for $C_{12}H_{20}O$: C, 79 94; H, 11.18. Found: C, 79.90; H, 11.04.

Registry No.—**5**, 18294-87-6; **6**, 3212-77-9; **7**, 39163-38-7; **8**, 41894-76-2; **14**, 41894-77-3; **15**, 41915-67-7; **16**, 41915-68-8; **17**, 41915-69-9; **19**, 41894-78-4; **20**, 41915-70-2; **21**, 41915-71-3; **22**, 41915-72-4; **23b**, 41915-73-5; **26**, 41894-79-5; **26** methyl ester, 41894-80-8; **27**, 41894-81-9; **27** methyl ester, 41894-82-0; **28**, 41894-83-1; **29**, 41894-84-2; **29** methyl ester, 41894-85-3; **30**, 41894-86-4; **30** methyl ester, 41894-87-5; **31**, 41894-88-6; bicyclo[4.3.0]non-6-ene-7-acetonitrile, 41894-89-7; tetrahydro-1-indanone, 22118-00-9; cyanoacetic acid, 372-09-8; bicyclo[4.3.0]nonene-2-acetonitrile, 41894-91-1; 4-hydrinanylidineacetonitrile, 41894-92-2; bicyclo[4.3.0]nonan-2-one, 5686-83-9; bicyclo[4.4.0]decene-2-acetonitrile, 41894-94-4; 1-decalinylidineacetonitrile, 41894-95-5; 1-decalone, 4832-16-0; bicyclo[3.3.0]-octene-2-acetonitrile, 41894-96-6; 1-octahydropentalenylideneacetonitrile, 41894-97-7; bicyclo[3.3.0]octan-2-one, 28569-63-3; tricyclo[7.2.1.0^{5,12}]dodecan-10-one, 41894-98-8; tricyclo[6.2.1.-0^{4,11}]undecan-3-ol, 41894-99-9; tricyclo[6.2.1.0^{4,11}]undecan-2-ol, 41895-00-5; tricyclo[7.2.1.0^{5,12}]dodecan-10-ol, 41895-01-6.

Thermal Cyclization of Substituted Aryl Propargyl Ethers. The Scope and Regioselectivity of the Reaction in the Synthesis of Substituted 3-Chromenes[1]

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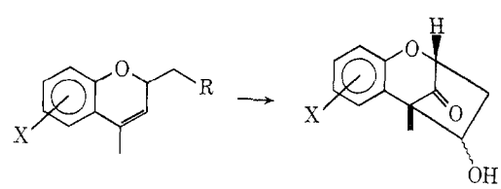
Received May 16, 1973

The thermal cyclization of substituted aryl propargyl ethers was examined. Simple 3-aryloxypropynes (**12**, **15a–c**) were cyclized to the corresponding chromenes in ~60% yield. The cyclization of **12** was not regiospecific and two isomeric chromenes (**13** and **14**) were obtained. The thermal cyclizations of C-1 and/or C-3 methyl-substituted 3-aryloxypropynes (**16d–g**) have been shown to proceed in a much higher yield than the corresponding unsubstituted compounds. The influence of water, reaction temperature, and solvent on the cyclization was also studied.

During the course of our research directed toward the synthesis of trichothecan mycotoxins and simpler analogs for antitumor evaluation, we required a simple yet flexible method for the synthesis of chromene precursors. Specifically, we required an efficient synthesis of 2,4-disubstituted chromenes (*cf.* eq 1) which



(1)

could incorporate a variety of substituents in the aromatic ring.

A variety of standard methods for the preparation of 3-chromenes have been described in the literature.[2] More recently, new methods have been developed; some of these newer methods include the reaction of vinylphosphonium salts with *o*-hydroxybenzaldehyde,[3] the oxidative cyclization of *o*-allyl phenols,[4] and the partial reduction of a coumarin followed by alkylation and cyclization.[5] None of these methods, however, appear to be broadly applicable and many suffer from the disadvantage of low yields, difficult and/or expensive reagents, and long procedures or difficult work-up.

The thermal cyclization of aryl propargyl ethers has been reported to yield chromenes and related compounds.[6–8] The general utility and scope of a variety of thermal reactions in organic synthesis (*e.g.*, Diels–Alder reaction, Claisen rearrangement, Cope rearrangement, etc.) prompted us to further examine this method for the synthesis of chromenes.

The Claisen rearrangement of propargyl ethers has been reported in both aromatic and nonaromatic systems.[9] Thermal cyclization of aryl propargyl ethers has been used to prepare naphtho[2,1-*b*]- and -[1,2-*b*]-pyrans,[6] pyranoflavones,[7d] pyranocoumarins,[7d,g] pyranoacridones,[7e] chromenes,[7] pyrano[3,2-*d*]pyrimidines,[8a] and furo[3,2-*d*]pyrimidines.[8a]

The mechanism of the thermal cyclization of aryl propargyl ethers has been studied by Zsindely and Schmid.[8b] The proposed mechanism (Scheme I) involves an initial Claisen rearrangement of the aryl propargyl ether **1** to give the allene intermediate **2**. Enolization of **2** followed by a [1,5] sigmatropic hydrogen shift would give **4**, which can undergo an electrocyclic reaction to give 3-chromene (**5**).[8b]

Otter, *et al.*, have proposed a similar mechanism (Scheme II) for the cyclization of uracil propargyl

(1) This research was supported by Grant 1 R01 CA 11880 from the National Cancer Institute, National Institutes of Health.

(2) (a) S. Wawzonek in "Heterocyclic Compounds," Vol. 2, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1951, pp 277–342; (b) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963, pp 220–250.

(3) E. E. Schweizer, A. T. Wehman, and D. M. Nycz, *J. Org. Chem.*, **38**, 1583 (1973), and references cited therein.

(4) G. Cardill, R. Cricchio, and L. Merlino, *Tetrahedron*, **27**, 1875 (1971).

(5) C. E. Cook and C. E. Twine, Jr., *Chem. Commun.*, 791 (1968).

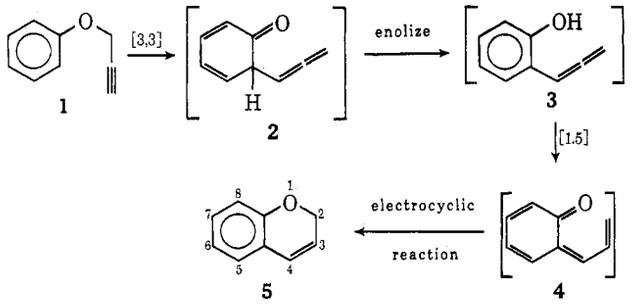
(6) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **10**, 926 (1962).

(7) (a) K. C. Majumdar and B. S. Thyagarajan, *J. Heterocycl. Chem.*, **9**, 489 (1972); (b) B. S. Thyagarajan, K. K. Balsubramanian, and R. Bhima Rao, *Tetrahedron*, **23**, 1893 (1967); (c) *Tetrahedron Lett.*, 1393 (1963); (d) J. Hlubucek, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **24**, 2347 (1971); (e) J. Hlubucek, E. Ritchie, and W. C. Taylor, *ibid.*, **23**, 1881 (1970); (f) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11**, 1042 (1963); (g) J. Nickl, *Chem. Ber.*, **91**, 1371 (1958).

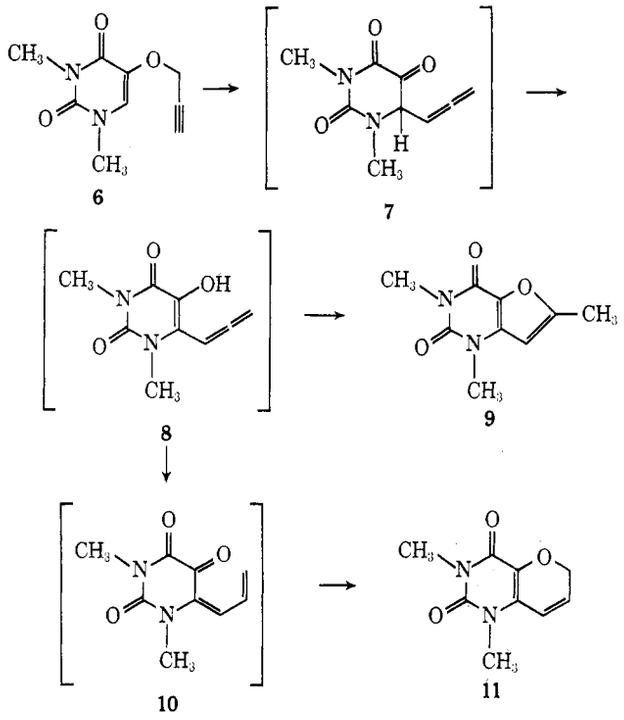
(8) (a) B. A. Otter, S. S. Saluja, and J. J. Fox, *J. Org. Chem.*, **37**, 2858 (1972); (b) J. Zsindely and H. Schmid, *Helv. Chim. Acta*, **51**, 1510 (1968).

(9) A. Jefferson and F. Scheinmann, *Quart. Rev., Chem. Soc.*, **22**, 391 (1968).

SCHEME I



SCHEME II



ethers (*e.g.*, **6**).[8a] In this case, however, both pyrimidopyrans (**11**) and furans (**9**) were formed. The greater electron-withdrawing effect of the uracil, as compared to the phenyl ring, was cited as a possible reason for the formation of the furo[3,2-*d*]pyrimidine (**9**). The electron-withdrawing effect of the uracil ring would make the central allenic carbon in **8** relatively electron deficient (compared to **3**) and hence more susceptible to nucleophilic attack of the enolic hydroxyl to give the furo compound (**9**).[8a] It should be noted that no benzofuran products have been reported from the thermal cyclization of phenyl propargyl ethers.[10]

Steric and electronic effects also appear to play a prominent role in the cyclization of aryl propargyl ethers (**1**) to 3-chromenes (**5**). In this regard aryl phenylpropargyl ethers[6,7f] and aryl 2,2-dimethylpropargyl ethers[7d,e] can be cyclized to the corresponding 4-phenyl-3-chromenes and 2,2-dimethyl-3-chromenes in yields superior to those obtained from simple aryl propargyl ethers.

(10) (a) Small quantities of benzofurans have been isolated in the red mercuric oxide–glacial acetic acid–sulfuric acid cyclization of phenyl propargyl ethers.[8a] The formation of benzo[*b*]thiophenes has been noted in the thermal cyclization of phenyl propargyl sulfides.[10b] (b) H. Kwart and T. J. George, *Chem. Commun.*, 433 (1970). (c) See also ref 9b and 10d. (d) R. Gaertner, *J. Amer. Chem. Soc.*, **73**, 4400 (1951).

With meta-substituted aryl propargyl ethers, cyclization is reported to occur regioselectively para to the substituent[7d,f] and electron-donating meta substituents have been reported to increase the yield of chromenes in the cyclization reaction.[7f,11]

The reported[7f] low yield for the syntheses of **13** (12.5% from **12**), **16a** (11.9% from **15a**), and **16b** (30% from **15b**) initially prompted us to repeat these experiments in an attempt to improve the yield to a point where this cyclization would become a synthetically useful reaction. The reactions were repeated as described in the literature, with the exception that they were carried out under a nitrogen atmosphere. The isolated yield of chromenes was in the range of 50–60%[12] (Table I). Furthermore, the cyclization of **12**

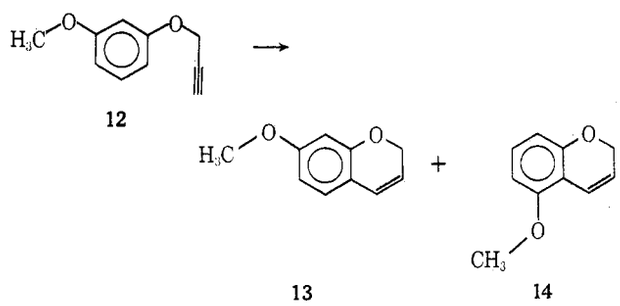
TABLE I

YIELDS OF SUBSTITUTED 3-CHROMENES (16) FROM SUBSTITUTED ARYL PROPARGYL ETHERS (15)

Compd	X (C-8)	Y (C-6)	R (C-2)	R′ (C-4)	Yield, %
16a[a]	H	OCH_3	H	H	60
16b[a]	OCH_3	H	H	H	58
16c[b]	$COCH_3$	H	H	H	65
16d[c]	H	OCH_3	H	CH_3	88
16e[b]	OCH_3	H	H	CH_3	83
16f[b]	H	OCH_3	CH_3	H	90
16g[b]	H	OCH_3	CH_3	CH_3	90

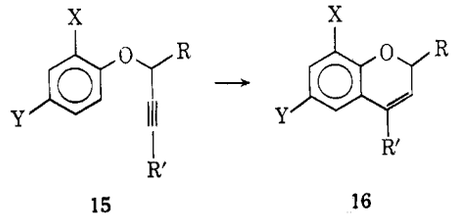
[a] See ref 7f. [b] Satisfactory combustion analytical data (±0.4%) were reported: Ed. [c] J. Colonge and A. Guyot, *Bull. Soc. Chim. Fr.*, 325 (1958).

led to the formation of *two* isomeric chromenes, **13** and **14**, in a ratio of approximately 46:54. This is in con-



trast with previous reports, wherein only **13** was reported as a product in the thermal cyclization of **12**.

In an effort to rationalize the discrepancy between our yields and the reported literature values we examined the effect of water added to the reaction mixture. In this regard *N*,*N*-diethylaniline was thoroughly dried and distilled immediately prior to its use in the reaction. The cyclization of **15a** (2.0 g) was



(11) Electronic effects have also been observed in the Claisen rearrangement of phenylallyl ethers; see ref 8b and 9 and references cited therein.

(12) The cyclization of **15a** was repeated in the absence of nitrogen and gave only slightly lower yield (43%).

carried out under anhydrous conditions and, in separate experiments, with 0.05 and 0.5 ml of water added to the *N,N*-diethylaniline (10 ml). The isolated yields of pure **16a** were 48, 54, and 39%, respectively.

The cyclization of **15a** (2.0 g) was also conducted in anhydrous *p*-diisopropylbenzene (10 ml) at 210–215°[13] and in *p*-diisopropylbenzene with 0.05, 0.25, and 1.0 ml of added water. The isolated yields of pure **16a** were 34, 44, 46, and 27%, respectively.

The effect of water on the cyclization thus appears to be minimal (in the case of either *N,N*-diethylaniline or *p*-diisopropylbenzene). A trace of water appears to facilitate the reaction somewhat. The most critical factor appears to be the reaction temperature. A *constant* bath temperature of 210–215° currently has proven most successful.

The yield of **16** is markedly increased in the cyclization of aryl propargyl ethers where the propargyl moiety is substituted (**15d–g**). These results are consistent with those of Hlubucek, *et al.*,[7d,e] where it was found that 2,2-dimethylchromenes were formed in high yield from the corresponding aryl propargyl ether.

The reasons for the increased yield in the cyclization of **15d–g** are not clear. It would seem unlikely that the methyl substituent(s) would have any reaction-promoting effect on the initial Claisen rearrangement or the subsequent enolization step. If subsequent steps are irreversible and non-rate-limiting the reactivity of either **3** or **4** should be of no consequence to the yield of **5** except as they allow escape from this reaction pathway to form different products.

Increased substitution on the propargyl moiety of **1** could stabilize the s-cis conformation of **4** (*i.e.*, destabilize the s-trans conformation *via* steric interactions) necessary for the final electrocyclic reaction (Scheme I). In this manner a smaller population of **4** in the s-trans conformation could result in fewer side reactions deriving from that non-product-yielding conformation.

Increased methyl substitution could also render the aryl propargyl ether (**1**) or the product chromene (**5**) more stable. In this regard a terminal acetylene, *e.g.*, **16f**, might be expected to exhibit a greater propensity toward polymerization than a less reactive nonterminal acetylene, *e.g.*, **16g**; however, both **16f** and **16g** afforded high yields (90%) of the respective chromenes under identical conditions. Thus the presence or absence of a terminal acetylene cannot be a major determinant of yield insofar as starting material stability is concerned. Similarly, the stability of the product chromenes does not appear to be significantly affected by increased methyl substitution.

If, on the other hand, the Claisen rearrangement or the subsequent enolization step is not rate limiting, then the reactivity of the allene intermediate, **3**, becomes a major determinant. The reactivity of allenes toward central attack by free radicals, nucleophiles, and electrophiles is known to increase with increasing methyl substitution on the allene moiety.[14] While the precise steric and electronic requirements for the hydrogen shift are not known, it would not be unreasonable to presume that this reaction would also be enhanced by increased methyl substitution on the allenic intermediate, **3**.

The thermal cyclization of substituted aromatic propargyl ethers to 3-chromenes can incorporate a variety of substituents at every position except C-3. Highest yields in this cyclization are achieved when the propynyl moiety is monosubstituted either at C-1 or C-3, disubstituted at C-3, and monsubstituted at both C-1 and C-3. The ready availability of a variety of phenols and propargyl halides makes this method a very attractive approach for the synthesis of a great variety of substituted 3-chromenes.

Iwai and Ide have reported that a resonance electron-donating meta substituent facilitated the cyclization of aryl proparyl ethers to 3-chromenes.[7f] In our work it is interesting to note the slightly higher yield obtained in the cyclization of **15c** (*p*-$COCH_3$ substituent) compared to **15b** (*p*-OCH_3 substituent). It should be noted that per cent yield cannot justify statements regarding reaction mechanisms, since the yield depends upon many factors including product stability and isolation. Furthermore, one cannot exclude, *a priori*, the possibility that various substituents simply retard competing decomposition reactions.

Further work is in progress to elucidate the effects of electron-donating and electron-withdrawing substituents on the aromatic ring and to study factors which influence the regioselectivity in the reaction.

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 data were determined in 95% ethanol solution on a Beckman DB-G grating spectrophotometer. The purity of analytical and spectral samples was confirmed by glc (Varian Aerograph Model 90-P with a thermal conductivity detector) using a 12-ft 30% NPGA column. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

General Procedure for Preparation of Aromatic Propargyl Ethers *via* Direct Williamson Etherification (Method A).—A mixture of the appropriate phenol (1.0 mol), the acetylenic halide (0.9 mol), and anhydrous K_2CO_3 (1.2 mol) in 400 ml of reagent-grade acetone was heated under reflux with vigorous stirring. The cooled mixture was filtered, and the inorganic residue was dissolved in H_2O (500 ml) and extracted with ether (2 × 50 ml). The filtrate was concentrated *in vacuo* and the residue was dissolved in ether (350 ml). The combined ethereal solution was washed with 5% NaOH solution (until pH of the ethereal layer gave a neutral reaction to moist pH paper), then H_2O (200 ml). The ether solution was dried (anhydrous Na_2SO_4) and concentrated *in vacuo*. The residue was distilled under vacuum (see Table II).

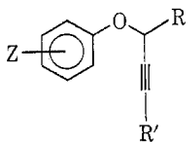
General Procedure for Preparation of Aromatic Propargyl Ethers *via* Alkylation of the Terminal Acetylene (Method B).—The appropriate acetylenic ether (0.1 mol) was added over a period of 10 min to a magnetically stirred suspension of $NaNH_2$ (0.1 mol) in liquid NH_3 (*ca.* 100 ml). The reaction mixture was stirred for 1 hr before methyl iodide (0.1 mol) was added over a period of 0.5 hr under an argon atmosphere (the argon was bubbled into the reaction mixture through a dispersion tube). The reaction mixture was cooled with a Dry Ice–acetone bath and let stand overnight. The residue was poured onto crushed ice (200 g) and extracted with ether (2 × 125 ml). The ethereal layer was washed with a saturated NH_4Cl solution and dried (anhydrous $MgSO_4$). The ethereal solution was concentrated *in vacuo* and the residue was vacuum distilled (see Table II).

(13) (a) At a temperature of 178–180° **15a** decomposed (polymerization) and no cyclized product was obtained. This is consistent with the results of Powell and Adams,[13b] who were unable to cyclize phenyl propargyl ether or *p*-bromophenyl propargyl ether in refluxing diisoamyl ether (bp 170°). (b) S. G. Powell and R. Adams, *J. Amer. Chem. Soc.*, **42**, 646 (1920).

(14) M. C. Casserio in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 239–299.

TABLE II

PREPARATION OF SUBSTITUTED ARYL PROPARGYL ETHERS 12 AND 15



Compd	Z	R	R′	Bp, °C (mm)	Yield,[a] %	Reaction time, hr
12[b]	*m*-OCH_3	H	H	86–87 (1.0)	83 (A)	17.5
15a[b]	*p*-OCH_3	H	H	82.5–83 (0.6)	89 (A)	13
15b[b]	*o*-OCH_3	H	H	83 (0.8)	84 (A)	20.5
15c[c]	*o*-$COCH_3$	H	H	96 (0.7)	76 (A)	15
15d[d]	*p*-OCH_3	H	CH_3	104 (0.9)	73 (A)	14
15d	*p*-OCH_3	H	CH_3	97.5–98 (0.8)	92 (B)[e]	
15e[c]	*o*-OCH_3	H	CH_3	126 (3.5)	77 (B)[e]	
15f[c]	*p*-OCH_3	CH_3	H	93 (1.5)	67.2 (A)	15[f]
15g[c]	*p*-OCH_3	CH_3	CH_3	77.5 (0.1)	75.1 (B)[e]	

[a] A or B in parentheses following the yield refers to method A or method B. [b] See ref 7f. [c] Satisfactory combustion analytical data (±0.4% for C, H) were provided: Ed. [d] W. N. White and B. E. Norcross, *J. Amer. Chem. Soc.*, **83**, 1968 (1961). [e] Unreacted terminal acetylene was removed with 5% ethanolic silver nitrate. [f] The reaction stood for 24 hr at room temperature prior to the 15 hr of heating.

General Procedure for Preparation of 3-Chromenes *via* Aromatic Propargyl Ethers.—A solution of the appropriate phenyl propargyl ether in *N*,*N*-diethylamine (distilled; 5 ml/g of phenyl propargyl ether) was heated to 210–215° under a nitrogen atmosphere without stirring. The *N*,*N*-diethylaniline was removed by distillation under a 1-mm vacuum, and further distillation under high vacuum yielded the desired chromenes (in the final stages of the distillation the bath temperature was increased *ca.* 80° above the boiling point of the chromene in order to remove last traces of product from the polymeric pot residue). Reported yields are based upon reaction with at least 5.0 g of starting acetylene.

7-Methoxy-Δ³-chromene (13) and 5-methoxy-Δ³-chromene (14) had 15-hr reaction time; 51% yield; bp 86–87° (1.0 mm); the isomeric mixture was separated by preparative glc (30% NPGA, 12 ft × 0.375 in. column at 190° with 35-μl injections) to yield **13** and **14** with retention times of 32.5 and 27.5 min, respectively.

7-Methoxy-Δ³-chromene (13) had ir 1271 (m), 1026 (m), 981 (s), and 758 cm^{-1}; uv max 226 nm (ε 17800), 286 (6640), and 306 (5750); nmr δ 3.67 (s, 3), 4.65 (d of d, 2, $J_{2,4}$ = 1.7, $J_{2,3}$ = 3.3 Hz), 5.52 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.28 (pair of t, 1), and 6.16–6.82 (m, 3). *Anal.* Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 74.17; H, 6.29.

5-Methoxy-Δ³-chromene (14) had ir 1059 (m), 1014 (m), 885 (w), 763 (m), 740 (s), and 680 cm^{-1} (w); uv max 232 nm (ε 16,900) and 282 (6790); nmr δ 3.72 (s, 3), 4.63 (d of d, 2, $J_{2,4}$ = 1.7, $J_{2,3}$ = 3.3 Hz), 5.58 (pair of t, 1, $J_{3,4}$ = 9.5 Hz), 6.65 (pair of t, 1), and 6.14–7.04 (m, 3).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.67; H, 6.19.

6-Methoxy-Δ³-chromene (16a) had 15-hr reaction time; 60.1% yield; bp 72–72.5° (0.18 mm); ir 1047 (s), 1035 (s), 811 (m), 754 (m), 709 (m), and 686 cm^{-1} (m); uv max 241 nm (ε 9920), 269 (2025), and 333 (3910); nmr δ 3.72 (s, 3), 4.71 (q, 2, $J_{2,4}$ = 1.7, $J_{2,3}$ = 3.5 Hz), 5.73 (pair of t, 1, $J_{3,4}$ = 10 Hz), 6.44 (pair of t, 1), and 6.36–6.65 (m, 3).

8-Methoxy-Δ³-chromene (16b) had 15-hr reaction time; 58.3% yield; bp 68° (0.1 mm); ir 1037 (m), 1020 (m), 794 (m), 766 (m), and 686 cm^{-1} (m); uv max 228 nm (ε 16,000), 273 (5030), 280 (4800), and 310 (803); nmr δ 3.77 (s, 3), 4.77 (d of d, 2, $J_{2,4}$ = 2, $J_{2,3}$ = 3 Hz), 5.71 (pair of t, 1, $J_{3,4}$ = 10 Hz), 6.34 (pair of t, 1), and 6.20–6.90 (m, 3).

8-Aceto-Δ³-chromene (16c) had 15-hr reaction time; 64.6% yield; bp 102° (0.6 mm); ir 1675 (s), 1053 (m), 814 (m), 752 (m), and 706 cm^{-1} (m); uv max 245 nm (ε 10,350) and 334 (3190); nmr δ 2.52 (s, 3), 4.90 (d of d, 2, $J_{2,4}$ = 1.9, $J_{2,3}$ = 3.6 Hz), 5.78 (pair of t, 1, $J_{3,4}$ = 10 Hz), 6.43 (pair of t, 1), 6.67–7.16 (m, 2), and 7.54 (pair of d, 1).

4-Methyl-6-methoxy-Δ³-chromene (16d) had 24.5-hr reaction time; 88% yield; bp 112.5° (2.2 mm); ir 1054 (m), 1008 (m), 824 (w), 799 (m), 774 (w), 732 (w), 705 (m), and 693 cm^{-1} (w); uv max 224 nm (ε 4020), 242 (6500), 266 (1400), and 331 (3440); nmr δ 2.00 (d of d, 3, $J_{4',3}$ = 1.8, $J_{4',2}$ = 1.3 Hz), 3.75 (s, 3), 4.63 (m, 2), 5.53 (m, 1), and 6.62 (s, 3).

4-Methyl-8-methoxy-Δ³-chromene (16e) had 24.5-hr reaction time; 83.0% yield; bp 114.5° (1.1 mm); ir 1038 (m), 1000 (m), 861 (m), 800 (m), 773 (w), 731 (m), and 661 cm^{-1} (w); uv max 236 nm (ε 7850), 276 (4910), and 316 (1680); nmr δ 1.98 (d of d, 3, $J_{4',3}$ = 2.0, $J_{4',2}$ = 1.4 Hz), 3.78 (s, 3), 4.61–4.81 (m, 2) 5.37–5.67 (m, 1), and 6.76 (s, 3).

2-Methyl-6-methoxy-Δ³-chromene (16f) had 12-hr reaction time; 89.5% yield; bp 86° (0.9 mm); ir 1050 (s), 871 (m), 851 (w), 817 (m), and 711 cm^{-1} (w); uv max 238 nm (ε 6270), 265 (1860), and 332 (2560); nmr δ 1.46 (d, 3, $J_{2',2}$ = 6.4 Hz), 3.77 (s, 3, 4.70–5.14 (m, 1), 5.67 (d of d, 1, $J_{3,4}$ = 9.6, $J_{3,2}$ = 3.0 Hz), 6.34 (d, 1), 6.50 (s, 1), and 6.67 (d, 2).

2,4-Dimethyl-6-methoxy-Δ³-chromene (16g) had 12-hr reaction time; 89.8% yield; bp 97° (1.1 mm); ir 1042 (s), 1031 (m), 852 (m), 811 (m), 769, and 690 cm^{-1} (m); uv max 239 nm (ε 10,580, 268 (2830), and 332 (3850); nmr δ 1.36 (d, 3, $J_{2',2}$ = 6.8 Hz), 2.00 (apparent t, 3), 3.73 (s, 3), 4.60–5.0 (m, 1), 5.40–5.57 (m, 1), and 6.66 (s, 3).

Registry No.—**12,** 41580-72-7; **13,** 18385-89-2; **14,** 41580-69-2; **15a,** 17061-86-8; **15b,** 41580-71-6; **15c,** 41580-73-8; **15d,** 41580-74-9; **15e,** 41580-75-0; **15f,** 33143-82-7; **15g,** 41580-77-2; **16a,** 18385-84-7; **16b,** 16336-25-7; **16c,** 41580-80-7; **16d,** 41580-81-8; **16e,** 41580-65-8; **16f,** 33143-98-5; **16g,** 41580-67-0.