J. Am. Chem. Soc., 85, 546 (1963); N. L. Allinger and L. A. Freiberg, ibid., 82, 2393 (1960); E. L. Eliel, Angew. Chem., Int. Ed. Engl., 4, 761 (1965).

(10) For discussion, see D. J. Loomes and M. J. T. Robinson, Tetrahedron, 33, 1149 (1977).

(11) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer, Model 257, infrared recording spectrophotometer fitted with a grating. The UV spectra were determined with a Cary, Model 14, or a Perkin-Elmer, Model 202, recording spectrophotometer. The ^1H NMR spectra were determined at 60 mHz with a Varian, Model T-60-A, NMR spectrometer and the ^{13}C NMR spectra were determined at 25 mHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi Perkin-Elmer, Model RMU-7, mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

Acid Catalysis of the Claisen Rearrangement. 2. Formation of the Benzofurobenzopyran and Benzofuro[3,2-*b*]benzofuran Skeletons from 1,4-Bis(aryloxy)-2-butynes

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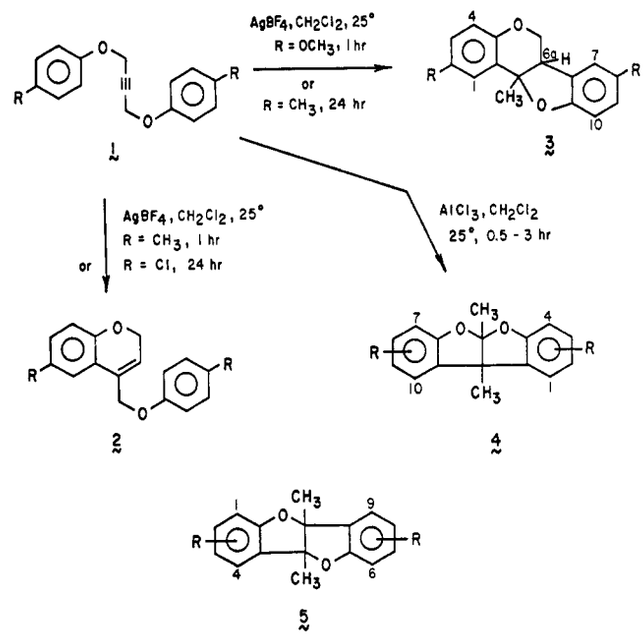
1,4-Bis(aryloxy)-2-butynes (1) can be selectively converted into 4-(aryloxymethyl)-2*H*-chromenes (2), 6*H*-benzofuro[3,2-*c*]-6a,11a-dihydro-11a-methylbenzopyrans (3), or 5a,10b-dihydro-5a,10b-dimethylbenzofuro[2,3-*b*]benzofurans (4) by treating a dichloromethane solution of 1 with mercuric trifluoroacetate, silver tetrafluoroborate, or anhydrous aluminum chloride, respectively. A mechanism involving charge-induced Claisen rearrangement triggered by π complex formation between the heavy metal ion and the C–C multiple bond (in 1 and 2) is postulated for formation of 2 and 3. Sequential charge-induced Claisen rearrangement of 1 into 3 by coordination of $AlCl_3$ with the oxygen atoms of 1 and 2 followed by ionic rearrangement of 3 into 4 is also postulated. The differing efficacy of metal ions in promoting isomerization of 1, 2, and 3 is discussed.

In a synthetic program designed to provide modified pterocarpin compounds related to pisatin, a phytoalexin isolated from stressed peas, *Pisum sativum* L., we required a covenient procedure for obtaining 6*H*-benzofuro[3,2-*c*]-6a,11a-dihydro-11a-methylbenzopyran derivatives (3). The reported[1] synthesis of such compounds involves Claisen rearrangement of 1,4-bis(aryloxy)-2-butynes. This procedure requires high temperatures (>200 °C) and long reaction times (~12 h).

Schmid[2] in a series of papers has reported that charge-induced Claisen rearrangements can be conducted at substantially lower temperatures and may show rate increases relative to the thermal process of up to 10^{10}. Two basic approaches to charge-induced Claisen rearrangements applicable to the case at hand have been described: (a) charge formation by heteroatom complexation with a hard[3] Lewis acid, e.g., BCl_3,[2] $ZnCl_2$,[4] H^+;[5] or (b) charge formation by coordination to C–C multiple bonds by soft Lewis acids, e.g., Ag^+,[6] Hg^{2+}.[7]

We therefore undertook a study of the reaction of 1,4-bis(aryloxy)-2-butynes with various hard and soft Lewis acids and now wish to report: (1) a very simple procedure for obtaining oxygen-substituted compounds 3 using silver tetrafluoroborate; and (2) a novel rearrangement of 1,4-bis(aryloxy)-2-butynes and isomers to 5a,10b-dihydro-5a,10b-dimethylbenzofuro[2,3-*b*]benzofurans (4) using anhydrous aluminum chloride (Scheme I).

Scheme I



Results

The conversion of phenyl propargyl ether into 2*H*-chromene by means of $AgBF_4$ in refluxing chloroform has been reported.[6] In attempts to extend this procedure to 1,4-bis(aryloxy)-2-butynes (1) we have found that the product obtained is a function of both the aryl group and the reaction time. The data are summarized in Table I. With activated aromatic rings 1 rearranges within 1 h into 3. Less activated compounds undergo rearrangement more slowly. Thus, **1d** gives the 2*H*-chromene **2d** while **1e** remains unchanged after 1 h at room temperature. After 24 h, however, **1d** gives **3d** and **1e** gives the 2*H*-chromene **2e**. For moderately activated compounds, i.e., **1b–d**, this is the method of choice for synthesis of 3.[8]

Silver trifluoroacetate is also an effective catalyst. Mercuric trifluoroacetate was less effective, rearranging only **1b** into the corresponding 2*H*-chromene. Aryl 2-propynyl ethers tolerate a broader range of substituents in the generation of 2*H*-chromene derivatives upon treatment with mercuric trifluoroacetate.[7b] Thallium trifluoroacetate was not a catalyst.

Examination of hard Lewis acids[9] revealed yet another

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Table I. Effect of Time and Substituent on the Rearrangement of 1 Catalyzed by $AgBF_4$[a]

	R (in 1)	registry no.	reaction time, h	product (% yield)	registry no.
a	2-OMe	4200-25-3	1	no reaction	
			24	no reaction	
b	4-OMe	4200-28-6	1	**3** (72)	41229-98-5
			24	**3** (61)	
c	3,4-OCH_2O	67238-29-3	1	**2** (59)	
d	4-Me	4200-18-4	1	**2** (55)	37113-57-8
			24	**3** (87)	14298-17-0
e	4-Cl	4200-26-4	1	no reaction	37104-73-7
			24	**2** (69)	

[a] Compound **1a** was very unreactive in all catalyst systems, being recovered unchanged after prolonged treatment with $Hg(O_2CCF_3)_2$ and only very slowly converted into **4** with $AlCl_3$. The predominant pathway was ether cleavage in the former reaction.

selective reorganization. Thus, treatment of a series of **1** with anhydrous $AlCl_3$ gave **4** in good to excellent yield (Table II).

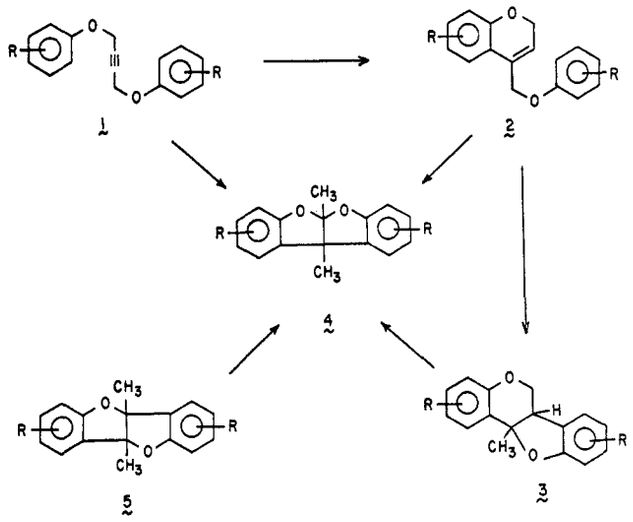
The assignment of structure **4** to these products rests on spectroscopic data and comparison of spectroscopic and physical data for **4b** and **4d** with data appearing in the literature.[11] We also assign the cis configuration to these compounds, as Dreiding models indicate the trans isomer is extremely strained.

In attempting to obtain more information about the **1** → **4** conversion we subjected various isomers of **1**, which we felt might be intermediates in the formation of **4**, to aluminum chloride in CH_2Cl_2. In all cases these isomers rearranged smoothly to **4**. Thus, treatment of **2g** and **3g** with $AlCl_3$ gave **4g** in 60 and 67% yield, respectively. Additionally, we prepared 4b,9b-dihydro-4b,9b-dimethyl-1,6-dichlorobenzofuro[3,2-*b*]benzofuran[12] (**5g**) and found that it also rearranges to **4** in the presence of $AlCl_3$ (although at a slower rate than **2** or **3**). The results are summarized in Scheme II.

Discussion

Transformation of **1** into **2** in the presence of HgO (acetic acid, 100 °C) has been reported[10] and attributed to acid-catalyzed cyclization of 1,4-diphenoxy-2-butanone (**6**) resulting from hydration of **1**. We have prepared several derivatives of

Scheme II



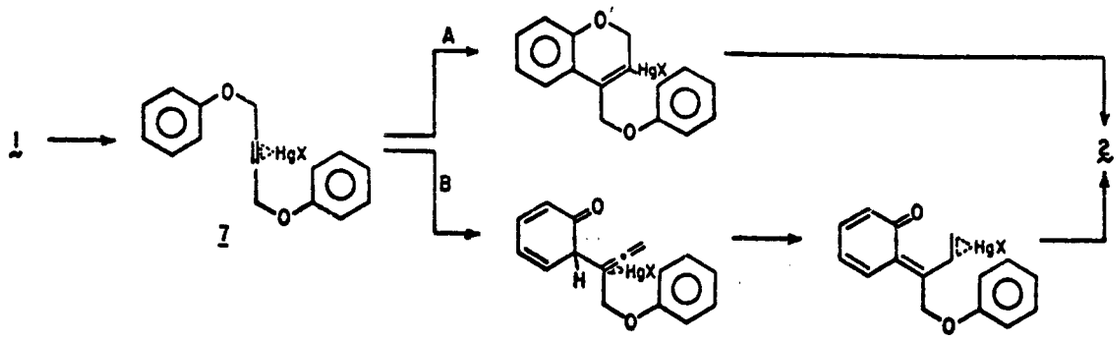
6 and find that none produce **2** when subjected to the cyclization conditions (either glacial acetic acid/HgO/100 °C or $CH_2Cl_2/Hg(O_2CCF_3)_2$/25 °C). An additional mechanism involving concerted sigmatropic rearrangement triggered by the charge induced by π-complex formation[13] can also be postulated (path B, Scheme III). Another possibility involving a σ complex, cyclization of this ion, and protonolysis of the C–Hg bond[14] (path A, Scheme III) produces a "two-step" sigmatropic mechanism[7a] which may be viewed as a metal ion catalyzed Friedel–Crafts alkenylation of an aromatic ring by an alkyne.[15,16] Path B represents a concerted sigmatropic process, paralleling that proposed by Schmid;[6] a large body of evidence for silver ion catalyzed sigmatropic rearrangement of phenyl propynyl ether has been published[6] and we have accumulated some related preliminary evidence pertaining to the sigmatropic nature of the mercuric ion catalyzed counterpart. Full discussion of this data will be deferred to a subsequent report. Two indirect points may be advanced at this time to discredit path A. First of all, two σ complexes may form from **7**, resulting in either a five- or a six-membered ring-containing product depending on the site of localization of the (+) charge. We have never observed any benzofuranoid compounds in the crude reaction mixture even though they were sought. Additionally, 1-phenyl-4-(*p*-bromophenoxy)-1-butyne, which could cyclize to a dihydrobenzoxepin via a Friedel–Crafts type reaction, does not produce any dihydrobenzoxepin, but instead produces only 1-phenyl-4-(*p*-bromophenoxy)-1-butanone under a variety of reaction conditions (see Experimental Section). These findings point to the uniqueness of 2*H*-

Table II. Data for 5a,10b-Dihydro-5a,10b-dimethylbenzofuro[2,3-*b*]benzofurans (4)[a]

	R (in 1)	registry no.	yield, %	registry no. (4)	mp, °C	NMR (5a and 10b methyls only)
b	4-OMe[b]		74	67238-32-8	122–123[c]	1.72 (3 H, s), 1.63 (3 H, s)
d	4-Me		77	67238-33-9	195–196[d]	1.73 (3 H, s), 1.60 (3 H, s)
e	4-Cl		63	67238-34-0	187.5–189.5	1.77 (3 H, s), 1.67 (3 H, s)
f	4-NO_2,[e] 3-CF_3	67238-30-6				
g	2-Cl	4467-00-9	30[f]	67238-35-1	223–224	1.83 (3 H, s), 1.68 (3 H, s)
h	2,4-Cl_2	37104-62-4	27	67238-36-2	267–269	1.85 (3 H, s), 1.68 (3 H, s)
i	2-F	67238-31-7	30[g]	67238-37-3	179.5–180.5	1.85 (3 H, s), 1.72 (3 H, s)

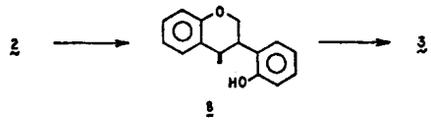
[a] In all cases examined the predominant mode of mass spectral fragmentation involves loss of methyl radical. Satisfactory analytical data were reported for all compounds. [b] In one run 10 mol % $AlCl_3$ was used, giving an 88% yield of **4b**. For less activated compounds this quantity of $AlCl_3$ gave a sluggish reaction. Yields in all reactions in this paper are not optimized. [c] Lit. mp 116 °C; NMR (methyl H's) δ 1.65 (3 H, s), 1.60 (3 H, s) [ref 11]. [d] Lit. mp 196–197 °C [K. Sisido, H. Nozaki, and T. Ilwako, *J. Am. Chem. Soc.*, **71**, 2037 (1949)]; 201–202 °C; NMR (methyl H's) δ 1.73 (3 H, s), 1.63 (3 H, s) [ref 11]. [e] Starting material recovered (80% recovery). [f] Purified by sublimation [150 °C (0.66 Torr)] followed by recrystallization from petroleum ether (60–110 °C). [g] Purified by sublimation [130 °C (0.8 Torr)].

Scheme III



chromene formation. We hold that this uniqueness is due to the intervention of a sigmatropic process as shown in path B (Scheme III) which, by virtue of the mechanism, can lead only to 2*H*-chromenes. Thus, the lack of five-membered rings from 1 and the hydration of 1-phenyl-4-(*p*-bromophenoxy)-1-butyne are readily accommodated. The apparent hydration reaction leading to the butanone derivative most probably involves hydrolysis of an intermediate vinyl trifluoroacetate, either by fortuitous moisture during the reaction or during the aqueous workup.

Conversion of **2** into **3** seemingly does not involve a Friedel–Crafts type alkylation as the expected site of charge formation (and, therefore, the site of attachment of the aromatic ring in **2**) is the tertiary benzylic position, not the observed site.[23] Claisen rearrangement to **8** followed by ring



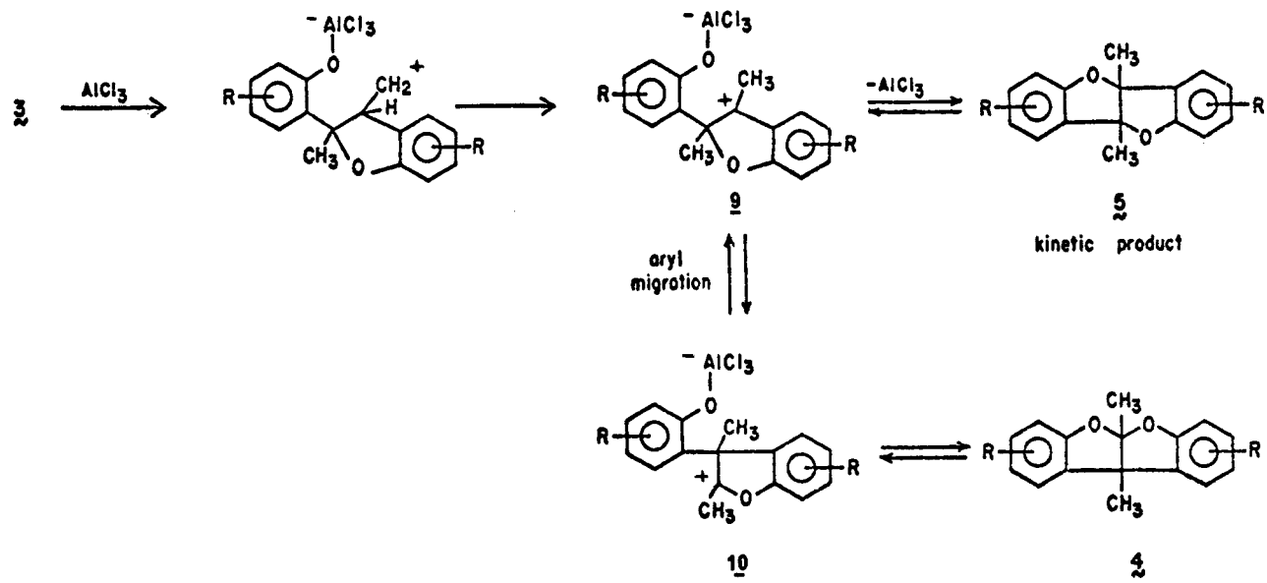
closure to **3** readily explains the site of attachment of the aromatic ring. 2-Allylphenols are well known to produce 2-methyl-2,3-dihydrobenzofurans under acidic conditions.[17,18]

Rearrangements of phenyl allyl ethers have been reported to be catalyzed by such hard Lewis acids as $TiCl_4$ and BF_3,[18c] which probably catalyze the reaction by coordination to the heteroatom. The present case is the first example of catalysis by a soft Lewis acid. This distinction is a very important one, as the site of coordination influences not only the efficacy of the catalyst but also the likelihood that the catalyst will induce other processes. For example, hard Lewis acids can promote not only Claisen rearrangement, but also ionic ring contraction as discussed below. In addition to Claisen rearrangement, soft Lewis acids may also promote double bond isomerization and/or migration.[18c]

It should be pointed out that the differing efficacy of Ag(I) and Hg(II) in rearranging alkene and alkyne substrates demonstrates that these reagents are indeed interacting at the unsaturated sites. Although heavy metal–ether and heavy metal–arene complexes are well known,[19] these complexes cannot be responsible for catalytic activity, as one would expect no difference in reactivity of alkenes and alkynes or at best reactivity paralleling thermal behavior, i.e., more facile rearrangement of alkene substrates, a phenomenon contrary to our findings. The rate enhancement of rearrangement in these cases is actually due to the metal ions, as sodium tetrafluoroborate (and sodium trifluoroacetate) as well as fluoroboric acid (as the diethyl ether complex) and trifluoroacetic acid have no effect on **1b** under conditions in which the corresponding silver(I) and mercury(II) salts completely isomerize **1b**. The failure of Ag(I) and Hg(II) to promote rearrangement of **3** into **4** may be taken as evidence that the site of coordination of **1** with these species is not the oxygen atom (see below).

$AlCl_3$ Catalyzed Reactions. Although we have been unable to isolate or detect intermediates in the $AlCl_3$ catalyzed conversion of **1** into **4**, it is reasonable to assume that **1** proceeds to **4** in a stepwise manner via **2** and **3**.[20] These transformations may be charge-induced Claisen rearrangements similar in mechanism to the process reported for BCl_3.[2] A mechanism accounting for the transformation of **3** into **4** is proposed in Scheme IV. Aluminum chloride promoted ether

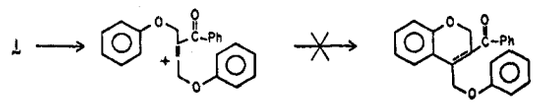
Scheme IV



cleavage in **3** would produce a primary cation which might be expected to readily rearrange to the more stable tertiary benzylic ion **9**. Kinetically controlled ring closure of **9** would produce **5**. However, in a thermodynamically controlled process the ion **9** may rearrange to **10**, which gives **4**, the apparent thermodynamic product, on ring closure.

Although neither the reaction of pterocarpin nor homopterocarpin (3,9-dimethoxy-6*H*-benzofuro[3,2-*c*]-6a,11a-dihydrobenzopyran) with aluminum chloride has been investigated, it is interesting that in the presence of aqueous HCl these compounds, which differ from **3** only by the absence of the 11a-methyl group, undergo fission of the five-membered ring, giving 2*H*-chromene derivatives.[21] We are in the process of examining the reaction of pterocarpins with aluminum chloride to understand this dichotomy.

The lack of formation of **4** in reactions conducted in the presence of soft Lewis acids may be readily explained. Formation of **4** most likely entails coordination of $AlCl_3$ with an oxygen atom, a hard base site. Since soft Lewis acids will have less propensity to coordinate with such sites, reactions involving soft acids should stop at **3**, as observed.



11

This interpretation is borne out by the fact that **1b** with $AgBF_4$ gives only **3b**, whereas the same reaction conducted in the presence of benzoyl chloride (presumably with $PhCO^+BF_4^-$ as the acid) produces **4** cleanly. Acylium ions are classified by Pearson[3] as hard acids. This result has additional significance because it provides some support for the assumption that hard acids are inducing rearrangement by coordination with a heteroatom rather than coordination with unsaturated sites. Benzoyl chloride has been reported[22] to undergo Friedel–Crafts reaction with a variety of alkynes in the presence of $AgBF_4$ or $AlCl_3$. If coordination in **1** was taking place at the triple bond, one would expect irreversible incorporation of the benzoyl function into the reaction product, i.e., **11**, a process we have not observed.

Research is in progress to further elucidate the mechanism of the conversion of **3** into **4** using deuterated samples, to extend the **1** → **4** conversion to the sulfur and nitrogen analogues of **1**, and to correlate the catalytic efficacy of metal salts to π complex stability constants.[25]

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are corrected. Spectral data were collected as follows: IR, crystallized melts unless otherwise specified, Perkin Elmer 435B; NMR, $CDCl_3$, Me_4Si reference (δ 0.00), Varian T-60; mass spectra, Varian M-77. Microanalyses were performed by Mr. Mike Gilles in the Michigan Technological University microanalytical laboratory.

The 1,4-bis(aryloxy)-2-butynes were prepared by standard methods and characterized by comparison of NMR and melting points to literature values. The following data were collected for new derivatives of **1**. 1,4-Bis[3-(trifluoromethyl)-4-nitrophenoxy]-2-butyne (**1f**): mp 94–95 °C (C_2H_5OH); NMR δ 8.15–7.95 (2 H, d, J = 9 Hz), 7.50–7.10 (4 H, m), 4.95 (4 H, s). Anal. Calcd for $C_{18}H_{10}F_6N_2O_6$: C, 46.57; H, 2.15; N, 6.03. Found: C, 46.48; H, 2.14; N, 5.94. 1,4-Bis(3,4-methylenedioxyphenoxy)-2-butyne (**1c**): mp 81–82 °C (C_2H_5OH); NMR δ 7.05–6.35 (6 H, m), 6.10 (4 H, s), 4.77 (4 H, s). Anal. Calcd for $C_{18}H_{14}O_6$: C, 66.26; H, 4.32. Found: C, 66.00; H, 4.30. The only new 2*H*-chromene prepared in this study was **2c**, which was obtained as a mixture of isomers that could not be conveniently separated: 59% yield; mp 190–210 °C (C_2H_5OH); NMR δ 6.80–6.40 (4 H, d), 6.00–5.95 (4 H, d), 4.68–3.75 (3 H, s superimposed on m), 2.25–2.00 (methyl H's, broad multiplet with spikes at 2.22, 2.15, 2.12, and 2.05). Anal. Calcd for $C_{18}H_{14}O_6$: C, 66.26; H, 4.32. Found: C, 66.02; H, 4.31. 2*H*-Chromenes for comparison samples were prepared by the method of Thyagarajan and Majumdar.[10]

General Procedure for the Reaction of 1 with Soft Lewis Acids. To the appropriate salt (0.5–1.0 molar equiv) in dichloromethane (~5 mmol/mL) was added, in one portion, solid **1**. After the reaction times indicated in Table I the reaction mixture was filtered through a pad of neutral alumina eluted with dichloromethane. The eluent was then concentrated in vacuo to give the product. Recrystallization of this material from petroleum ether (60–110 °C) gave the pure compound, identified by comparison (mp, IR, NMR) with authentic samples.

General Procedure for the Preparation of 4. To a stirred solution of **1** (3 g) in dichloromethane (50 mL), under N_2, was added in one portion an equimolar amount of $AlCl_3$. Immediately an intensely colored solution formed (usually green or red) and after a few minutes the reaction mixture began to gently reflux. After stirring an additional 30 min, 3 N HCl (25 mL) was cautiously (frothing) added. The organic layer was collected and washed successively with water (50 mL), 10% NaOH (50 mL), and again with water (50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo to give the products listed in Table II. Recrystallization from petroleum ether (60–110 °C) gave analytical samples.

Reaction of 1b with $AgBF_4$ and Benzoyl Chloride. To **1b** (1.5 g) in dichloromethane (30 mL), under N_2, was added benzoyl chloride (1 molar equiv) followed immediately by solid $AgBF_4$ (1 molar equiv). At this point some fluoroboric acid vapors were noted. The reaction mixture was then stirred (1–24 h, depending on **1**). The filtered reaction mixture (green to blue in color) was washed with 3 N HCl (25 mL) followed successively by water (50 mL), 10% KOH (25 mL), and water (50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo to give a 40% yield of **4b** identical in all respects with the material obtained in the $AlCl_3$ catalyzed reaction of **1b**.

Conversion of 3g and 5g into 4g. Compound **3g** (1.5 g) was added to a slurry of $AlCl_3$ (0.5 g) in CH_2Cl_2 (15 mL) under a blanket of N_2. A red color developed immediately and after 5 min the solution gently refluxed. After stirring 35 min the reaction mixture was quenched by cautious addition of 3 N HCl (organic phase became colorless) and worked up as above to give **4g** (67%). Similar reaction of **5g** also gave a blood red solution and an exotherm developed. Workup as above gave a quantitative yield of a solid containing ~85% **4g** and ~15% unreacted **5g** (by NMR integration).

Preparation of 1-Phenyl-4-(*p*-bromophenoxy)-1-butyne. To a solution of phenylacetylene (1.16 g, 0.0114 mol) in dry dioxane (20 mL) was added 4.6 mL of 2.48 M butyllithium (0.0114 mol in hexane). The mixture was heated to reflux and solid 2-(*p*-bromophenoxy)ethyl *p*-toluenesulfonate (4.12 g, 0.0111 mol) was added portionwise to the dark solution. Approximately 4 mL of liquid was distilled away; the remaining solution was refluxed for 11 h during which time a voluminous precipitate formed. The cooled mixture was diluted with water (100 mL) and extracted with ether (3 × 50 mL). The combined extracts were successively washed with water and brine, and the organic phase was then dried ($MgSO_4$). Solvent removal in vacuo gave a yellow oil which crystallized on standing (1.86 g, 56%). Recrystallization from hexane gave an analytical sample: mp 46.5–48 °C; IR (NaCl, melt) 3050, 2925, 1590, 1490, 1295, 1245, 1180, 1080, 1040, 1005, 830, 760, 700 cm^{-1}; NMR δ 7.33–7.00 (7 H, m), 6.57 (2 H, d, J = 9.0 Hz), 4.05 (2 H, t, J = 8.0 Hz), 2.77 (2 H, t, J = 8.0 Hz). Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.80; H, 4.36. Found: C, 63.85; H, 4.33.

Reaction of 4-(*p*-Bromophenoxy)-1-phenyl-1-butyne with Mercuric Trifluoroacetate. To a solution of 0.30 g (1.00 mmol) of 4-(*p*-bromophenoxy)-1-phenyl-1-butyne in dry (distilled from and stored over CaH_2) THF (2 mL) was added solid mercuric trifluoroacetate (0.44 g, 1.03 mmol) portionwise over 1 min. After stirring at room temperature for 1 h the solution was refluxed for an additional 4.5 h. The cooled solution was treated with 25 mL of an alkaline $NaBH_4$ solution (1 g of $NaBH_4$, 0.5 g of NaOH). The mixture was filtered and the filtrate was extracted with chloroform (2 × 50 mL). The combined chloroform extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The yellow oil thus obtained was purified by preparative layer chromatography (SiO_2/3:2 hexane–benzene), giving 55 mg of recovered starting material and 110 mg (42%) of the butanone: mp 71–72 °C (cyclohexane); NMR δ 8.2–6.6 (9 H, m), 3.93 (2 H, t, J = 6.0 Hz), 3.07 (2 H, t, J = 6.0 Hz), 2.13 (2 H, apparent quintet, J = 6.0 Hz). Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.18; H, 4.74. Found: C, 60.43; H, 4.68.

Repetition of this experiment in CH_2Cl_2 and in THF in the presence of acid or water scavengers (CaO, HgO, 4Å molecular sieves) altered the reaction rate but not the major product.

Reaction of 4-(*p*-Bromophenoxy)-1-phenyl-1-butyne with Mercuric Acetate. To a hot solution of 2.17 g (10 mmol) of HgO in 11 mL of glacial acetic acid was added 3.01 g (10 mmol) of 4-(*p*-bromophenoxy)-1-phenyl-1-butyne in glacial acetic acid (6 mL) over 5 min. After an additional 5 h of heating over a steam bath, the mixture

Table III. Relative Percentages of 2, 6, and 12 Produced by Hydration of 1[a]

substituent (in 1)	chromene	registry no.	6	registry no.	12	registry no.
4-OMe	100	67238-38-4	0		0	
2-OMe	100	38532-35-3	0		0	
2-Br[b]	18	37104-76-0	51	67238-39-5	31	67238-43-1
2-Cl	16	37104-72-6	56	67238-40-8	28	67238-44-2
4-Cl	11		52	67238-41-9	37	67238-45-3
2,4-diCl	0		84	67238-42-0	16	67238-46-4

[a] By integration of NMR spectrum of crude reaction mixture. Physical and spectral data for new compounds appear in Table IV. [b] Registry no.: 37104-64-6.

Table IV. Physical and Spectroscopic Data for 6 and 12[c]

R (in 1)	product	mp, °C	NMR (aromatic portion deleted)
2-Br	6	95–97	4.74 (2 H, s), 4.55–4.25 (2 H, t, J = 6 Hz), 3.35–3.05 (2 H, t, J = 6 Hz)
2-Cl	6	96–97	4.71 (2 H, s), 4.45–4.20 (2 H, t, J = 6 Hz), 3.30–3.00 (2 H, t, J = 6 Hz)
4-Cl	6	93–94	4.66 (3 H, s), 4.45–4.20 (2 H, t, J = 6 Hz), 3.20–2.95 (2 H, t, J = 6 Hz)
2,4-diCl	6	99–100	4.75 (2 H, s), 4.50–4.25 (2 H, t, J = 6.4 Hz), 3.30–3.00 (2 H, t, J = 6.4 Hz)
2-Br	12	[132–133 (0.007)][b]	4.57 (2 H, s), 3.85–3.60 (2 H, t, J = 6 Hz), 3.30 (3 H, s), 3.00–2.75 (2 H, t, J = 6 Hz)
2-Cl	12	[115 (0.004)][b]	4.60 (2 H, s), 3.85–3.55 (2 H, t, J = 6 Hz), 3.29 (3 H, s), 3.00–2.70 (2 H, t, J = 6 Hz)
4-Cl	12	27	4.63 (2 H, s), 3.85–3.60 (2 H, t, J = 6 Hz), 3.37 (3 H, s), 2.95–2.70 (2 H, t, J = 6 Hz)
2,4-diCl[a]	12	43–44	4.60 (2 H, s), 3.80–3.55 (2 H, t, J = 5 Hz), 3.28 (3 H, s), 2.95–2.65 (2 H, t, J = 5 Hz)

[a] Obtained from the corresponding 6 by refluxing in acidic methanol. [b] Boiling point (Torr). [c] Satisfactory analytical data were reported for the compounds.

was extracted with chloroform (2 × 100 mL). The combined chloroform extracts were washed with 10% K_2CO_3 solution until neutral and then with water (100 mL). The organic layer was dried ($MgSO_4$), the solvent was removed in vacuo, and the residue was chromatographed on SiO_2 to give 2.4 g (75%) of the ketone described above.

General Procedure for Hydration of 1. Mercuric oxide (6.75 g, 0.03 mol) was dissolved in a solution of concentrated sulfuric acid (5.3 mL) and water (20 mL). After stirring for about 5 min at 25 °C the solution was diluted with methanol (25 mL) [note: bright opaque yellow color formed]. The mixture was then heated to reflux and 1,4-bis(aryloxy)-2-butyne (1 molar equiv based on HgO) in tetrahydrofuran (60–80 mL) was then added in one portion. After 12–18 h at reflux, the cooled solution was filtered and evaporated in vacuo to one-tenth of the original volume. After dilution with water (1 L) and extraction with ether (3 × 150 mL), the combined organic phase was washed successively with water (100 mL), 5% potassium hydroxide solution (200 mL), and water (100 mL). Drying ($MgSO_4$) and solvent evaporation gave the crude product. The NMR spectrum was used to give the relative amounts of **2**, **6**, and 1-aryloxy-4-methoxy-2-butanones (**12**) indicated in Table III. Subsequent chromatography on silica gel eluted with hexane gave the chromene derivative. Elution with chloroform gave a mixture of **6** and **12** which was readily separated by refluxing in hexane (selectively dissolving the oily **12** from crystalline **6**). Recrystallization or distillation then gave analytically pure samples having the spectral and physical properties listed in Table IV. The 1-aryloxy-4-methoxy-2-butanones (**12**) arise from **6** presumably via an acid-catalyzed β elimination/Michael addition sequence. Prolonged reflux completely converts **6** to **12**.

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Registry No.—**2c** isomer I, 67238-47-5; **2c** isomer II, 67238-48-6; **3g**, 14270-20-3; **5g**, 3988-23-6; 1-phenyl-4-(*p*-bromophenyloxy)-1-butyne, 67238-49-7; phenylacetylene, 536-74-3; 2-(*p*-bromophenoxy)ethyl *p*-toluenesulfonate, 67238-50-0; 1-phenyl-4-(*p*-bromophenoxy)-1-butanone, 67238-51-1.

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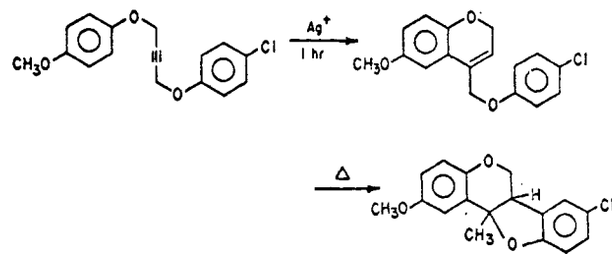
(8) This charge-induced process should allow one to selectively form **3** having the more electron rich aromatic residue fused to the 6-ring with the other aromatic residue fused to the 5-ring, e.g.,



Such selectivity is not possible in the direct thermal process due to the lack of a pronounced substituent effect in the Claisen rearrangement; cf. S. J. Rhodes and R. Rollins, *Org. React.*, **22**, 1 (1975).
(9) Iron(III) chloride was a less effective catalyst (in CH_2Cl_2), reacting slowly with **1b** to give **4b** as the sole product. Boron trifluoride etherate (in CH_2Cl_2) was even less effective, giving ~5% conversion to **4b** after 24 h. Zinc chloride was without effect on **1**, while $SbCl_5$ caused extensive, rapid decomposition to unidentified compounds.
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(16) (a) This process is isoelectronic with the Fodor modification of the Bischler–Napieralski reaction, i.e., transformation of nitrilium ions into 3,4-dihydroisoquinolines. (b) The Bischler–Napieralski reaction has been successfully applied to the formation of seven-membered rings [3,4-dihydro-5*H*-benzazepines, cf. Y. Kanaoka, E. Sato, O. Yonemitsu, and Y. Ban, *Tetrahedron Lett.*, **No. 35**, 2419 (1964)].
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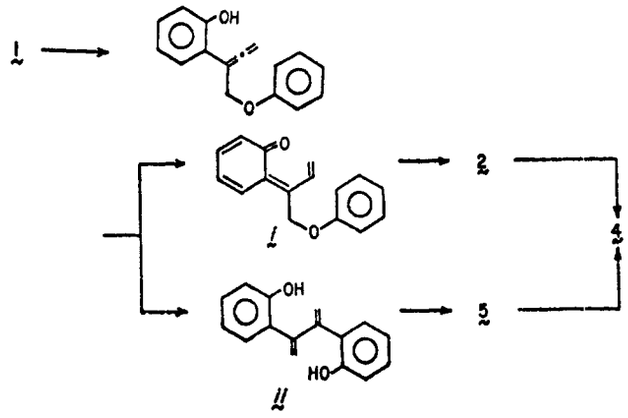
(18) Initial results indicate that phenyl allyl ether does not undergo similar rearrangement in the presence of $AgBF_4$ or $Hg(O_2CCF_3)_2$; however, this and similar cases are presently under investigation. Phenyl allyl ethers have available at least three alternative reaction modes in addition to Claisen rearrangement: (a) isomerization into thermodynamically more stable vinyl ethers [cf. J. M. Reuter and R. G. Salomon, *J. Org. Chem.*, **42**, 3360 (1977)]; (b) simple ether cleavage [J. F. W. McOmie, J. Watts, and D. West, *Tetrahedron*, **24**, 2289 (1968)]; and (c) Claisen rearrangement with [H. Hui and H. Yip, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2689 (1976)] or wi-

thout subsequent polymerization [K. Narasaka, E. Balk, and T. Mukaiyama, *Chem. Lett.*, 1041 (1975)]. The factors controlling reactivity of a substrate in any given reaction mode are unknown and at present the behavior of a given substrate under a particular set of reaction conditions cannot be predicted.

(19) (a) O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, **8**, 1953 (1954); (b) J. March, "Advanced Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1977, pp 79–80.

(20) An alternative mechanism involving direct formation of **5** from **1** by a "double" Claisen rearrangement followed by ionic rearrangement as shown below may be excluded from consideration. If this mechanism was operating one might expect to isolate **5** from reaction of **1** with heavy metal ions. Additionally, the absence of **5** in all crude $AlCl_3$ catalyzed reaction mixtures, even when the reaction was interrupted at low conversion, makes this path seem unlikely. It would appear that the 1,5-hydrogen shift leading to i is faster than the 3,3 process leading to ii. Schmid (ref 2) has indicated that the initial thermal rearrangement is slower than the 1,5-hydrogen shift in the rearrangement of phenyl propynyl ethers into 2*H*-chromenes.



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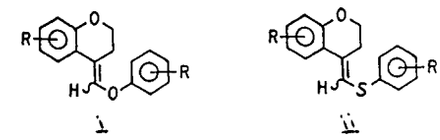
(23) As pointed out by a referee, the spirocyclic intermediate produced by the Friedel–Crafts process could be formed reversibly. On this basis it was suggested that the observed mode of fusion might ultimately prevail. However, under equilibrating conditions, formation of charge at the benzylic position would most probably result in formation of the vinyl ether, i, or



products derived from it (rather than from **2**). Support for this contention derives from the well-known thermodynamic stability of vinyl ethers over allyl ethers. Additionally, treatment of the related sulfur system ii with trifluoroacetic acid in refluxing chloroform produces the corresponding vinyl sulfide in excellent yield (ref 23b) presumably via a benzylic cation. We therefore do not consider formation of **2** by a Friedel–Crafts type alkylation likely. (b) B. S. Thyagarajan, K. C. Majumdar, and D. K. Bates, *J. Heterocycl. Chem.*, **12**, 59 (1975).

(24) Reactions at the triple bond of aryl 2-propynyl ethers have also been sought but not found. Thus, phenyl 2-propynyl ether reacts with $PhCO^+$ $AlCl_4^-$ producing 4-benzoylphenyl 2-propynyl ether in good yield. When the 4 position of the ether is blocked, ether cleavage producing the aryl benzoate occurs: unpublished observations of M. Dziobak, 1978.

(25) This paper is dedicated to the memory of Professor H. Schmid.

Reactions of Ketones with Sodium Hydride or Potassium Hydride in the Presence of Trimethylsilyl Chloride. Preparation of Trimethylsilyl Enol Ethers[1]

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Reactions of cyclohexanone with NaH and Me_3SiCl in various solvents yielded predominantly (90–97%) the silyl enol ether **2** resulting from enolization, with only a few percent of the alkyl silyl ether **1** resulting from initial reduction. Similar reactions with KH and Me_3SiCl proceeded well only in dioxane to give >99% of **2**. Cyclohexanone, 2-methylcyclohexanone, acetophenone, and 2-heptanone were converted to trimethylsilyl enol ethers in good yields by this method.

Alkali metal hydrides are widely used as bases in organic synthesis and have been especially useful for the conversion of carbonyl compounds to metal enolates.[3–5] Sodium hydride has been most commonly used.[3] Potassium hydride has recently been shown to be much more reactive than sodium hydride and is an excellent reagent for the generation of potassium enolates.[4] Lithium hydride, although comparatively unreactive, has been used in a few cases to generate lithium enolates.[5]

Some hydrides of other metals, particularly complex metal hydrides such as $NaBH_4$ and $LiAlH_4$, are widely used as reducing agents in organic synthesis;[6] these hydrides will usually reduce a carbonyl group rather than abstract an enolizable hydrogen. In contrast, alkali metal hydrides have been reported to reduce organic compounds relatively infrequently.[7–10] Reductions of carbonyl groups have been reported only in special cases; for example, sodium hydride has been shown to reduce carbonyl compounds which have no enolizable hydrogens or which are not readily enolized.[7]

The reactions of alkali metal hydrides with carbonyl compounds to give metal enolates are commonly believed to be catalyzed by alkoxides (formed from traces of alcohol impurities in the reaction mixtures) as the proton-transfer agents,[3c,i] since the hydrides are insoluble in common organic solvents.[4c,11] Thus, catalytic amounts of ethanol have been used to initiate sluggish reactions of metal hydrides.[3c,4e] We were intrigued by the possibility that the reactions of ketones with alkali metal hydrides might proceed by initial *reduction* of a small fraction of the ketone to the corresponding alkoxide, which would then catalyze enolate formation by acting as the proton-transfer agent (Scheme I). We have therefore studied the reactions of several ketones with sodium, potassium, and lithium hydrides in the presence of trimethylsilyl chloride, a reagent expected to trap enolate anions or alkoxide anions as they are formed.[12,13] To the extent that reduction takes place, an alkyl trimethylsilyl ether (e.g., **1**) should be formed; to the extent that direct enolization takes place, an alkenyl trimethylsilyl ether (trimethylsilyl enol ether, e.g., **2**) should be

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