Na_2SO_4. Filtration and concentration via rotary evaporation of the ether solution afforded an orange oil (2.74 g) which was distilled through a short-path column at 0.25 mm (bp 36–38 °C). A 2.14-g (0.0198 mol, 66%) fraction of **2** (white solid) was obtained which partially clogged the condenser and receiver elbow, mp 40.5–41.5 °C. GC analysis on the KOH-treated column showed the syn/anti ratio to be 2.2:97.8.

Preparation of Tosylhydrazones. The lability of **1** and **2** in the presence of acid precluded acid-catalyzed formation of the respective tosylhydrazones. The respective tosylhydrazones were prepared by stirring equimolar quantities of *p*-toluenesulfonyl hydrazide and the ketone in absolute ethanol (1 g/25 mL) for 21–24 h (25 °C). A notable exception was **1**, which within 5 min after mixing led to the precipitation of the desired tosylhydrazone; the resulting slurry was stirred for only 2 h before workup. The crude tosylhydrazone obtained from **2** upon removal of solvent was first chromatographed on silica gel (methylene chloride eluent) and then recrystallized from ethanol at 0 °C. The tosylhydrazone from **1** required only recrystallization from ethanol. *syn*-Tricyclo[4.1.0.0^{2,4}]heptan-5-one tosylhydrazone: 83% yield; mp 176.0–178 °C dec; IR (KBr) 3350, 3150, 1630, 1580 (sh), 1450, 1390, 1370, 1330, 1310, 1295, 1180, 1160 (s), 1085, 1040, 1015, 940, 900, 825, 810, 720, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (m, cyclopropyl methylene H, 4 H), 1.96 (m, cyclopropyl methine H, 4 H), 2.40 (s, CH_3, 3 H), 7.47 (s, –NH, 1 H), 7.58 (AB q, aromatic H, 4 H); MS *m/e* 276 (M^+), 91 ($C_7H_7^+$, major peak).

Anal. Calcd for $C_{14}H_{16}O_2N_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.84; N, 10.19.

anti-Tricyclo[4.1.0.0^{2,4}]heptan-5-one tosylhydrazone: 31% yield; mp 132–134 °C dec; IR (KBr) 3350, 3150, 2850, 1590 (sh), 1540, 1480, 1430, 1385, 1335, 1320, 1310, 1300, 1180, 1160 (s), 1085, 1025, 1010, 935, 895, 820, 805, 725, 715, 705 cm^{-1}; NMR ($CDCl_3$) δ 0.52 (m, cyclopropyl endo H, 2 H), 1.03 (m, cyclopropyl exo H, 2 H), 1.70 (m, cyclopropyl methine H, 4 H), 2.40 (s, CH_3, 3 H), 7.27 (s, –NH, 1 H), 7.58 (AB q, aromatic H, 4 H); MS *m/e* 276 (M^+), 91 ($C_7H_7^+$, major peak).

Anal. Calcd for $C_{14}H_{16}O_2N_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.82; H, 5.86; N, 10.17.

Registry No.—**1**, 67252-83-9; 1 tosylhydrazone, 67252-84-0; **2**, 28697-20-3; **2** tosylhydrazone, 67252-85-1; **8**, 53859-89-5; **9**, 67194-62-1; *cis*-**11**, 67194-63-2; *trans*-**11**, 67194-64-3; *cis*-**14**, 2183-92-8; *trans*-**14**, 2183-93-9; *cis*-**15**, 67194-65-4; *trans*-**15**, 67194-66-5; **18**, 32264-58-7; *cis*-7,8-bis(chloromethyl)-1,4-dioxaspiro[4.4]nonane, 67194-67-6; *trans*-7,8-bis(chloromethyl)-1,4-dioxaspiro[4.4]nonane, 67194-68-7.

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Chemistry of Carbanions. 33. Use of Intramolecular Alkylation for the Stereospecific Formation of a *cis*-Decalone[1]

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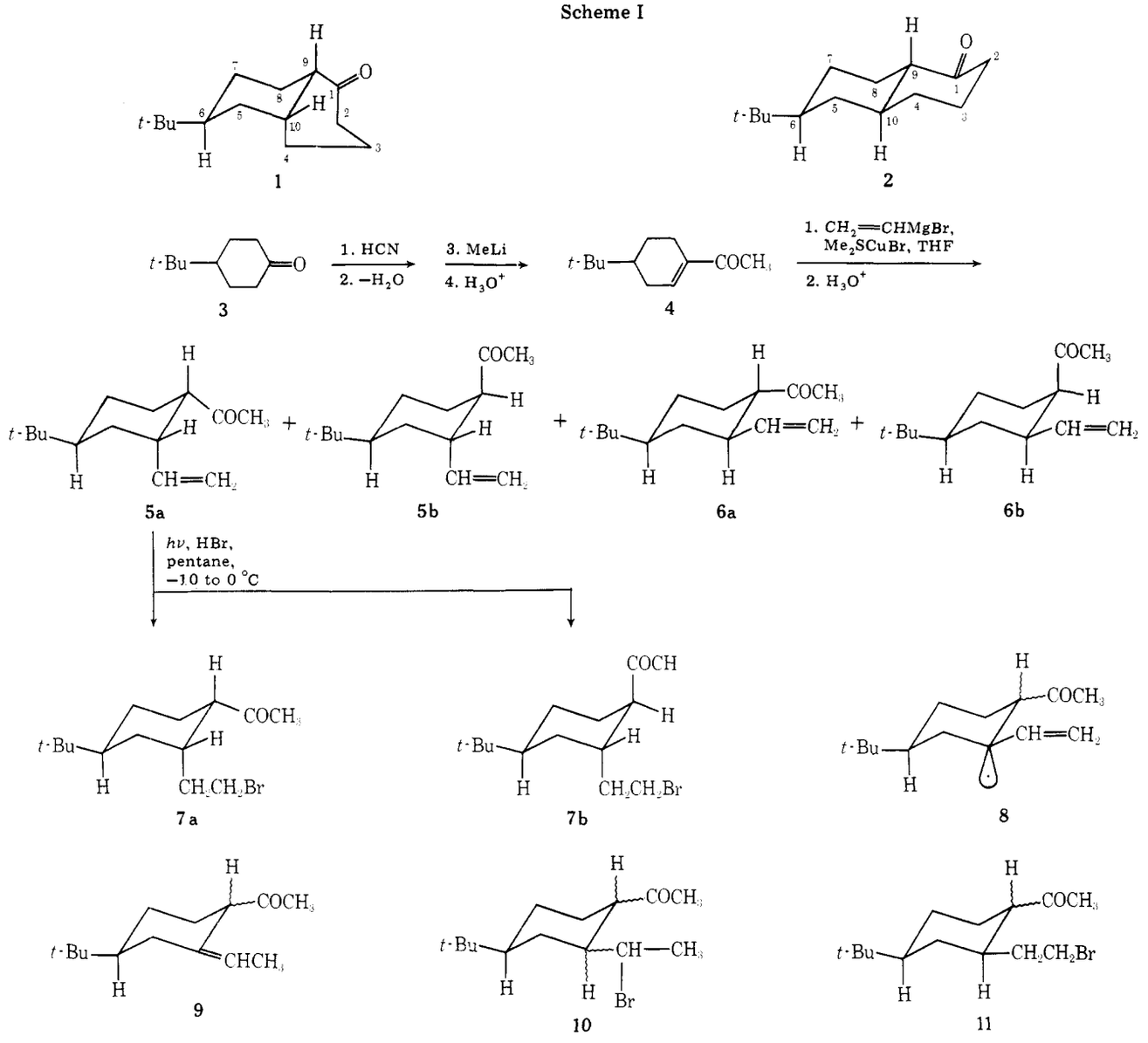
The synthesis of the decalone derivatives **1** and **14** and the related enol acetates **15** and **16** is described. This synthesis utilizes the stereoselective conjugate addition of CH_2=CHMgBr in the presence of a Cu(I) catalyst to form the vinyl ketone **5**. Subsequent addition of HBr in a radical chain reaction followed by regiospecific formation and cyclization of the bromo enolates **12** and **13** formed the desired decalones **1** and **14**.

To continue exploration of the possibility[2] of controlling reaction stereochemistry in polycyclic systems by use of a conformational effect transmitted from a remote bulky substituent, we wished to prepare ketone **1** (Scheme I). We plan to compare the stereochemistry of C-9 alkylation of this ketone **1** with an earlier study[3] of the alkylation of the stereoisomeric ketone **2**. This paper reports a suitable route for the preparation of ketone **1**.

The basic problem in this synthesis was the requirement to establish and maintain the two chiral centers at C-6 and C-10 in the less stable arrangement with the two alkyl groups trans (i.e., one alkyl group axial). Application of a standard Robinson annulation technique to 4-*tert*-butylcyclohexanone (**3**) was clearly inappropriate because equilibration during this process ultimately leads to the more stable ketone **2**.[3] Consequently, we used an alternative procedure[4,5a] in which the ketone **3** was converted to the enone **4** and then allowed to react with CH_2=CHMgBr in the presence of a Cu(I) catalyst (0.1 molar equiv of Me_2SCuBr). This organometallic reagent (CH_2=CHMgBr + 0.1 equiv of Me_2SCuBr) has been found[4b,5a] to react with enones in a manner equivalent to the cuprate, $(CH_2{=}CH)_2CuLi$, that is presently difficult to prepare because of the lack of a commercial source for vinyllithium. By use of these Cu(I) reagents, both methyl and vinyl groups have been found[4,5a] to add to the enone **4** to form mixtures of stereoisomeric ketones (e.g., **5** and **6**) in which the epimers (e.g., **5**) with an axial methyl or vinyl group constitute >90% of the ketone product. We had previously[5a] used a low-temperature recrystallization technique to separate a pure sample of ketone **5a**, the major stereoisomer in the reaction mixture, and have subsequently found that both epimers **5a** and **5b** can be obtained in pure form by low-pressure liquid chromatography. An equilibrium mixture of these two epimers contained ca. 70% of **5a** and ca. 30% **5b**.[4b,5a] Pure samples of the two minor epimeric ketones **6a** and **6b** were also separated by low-pressure liquid chromatography. An equilibrated mixture of these epimers **6** at 25 °C contained 99% of the equatorial isomer **6a** and 1% of the axial isomer **6b**.

0022-3263/78/1943-3851$01.00/0

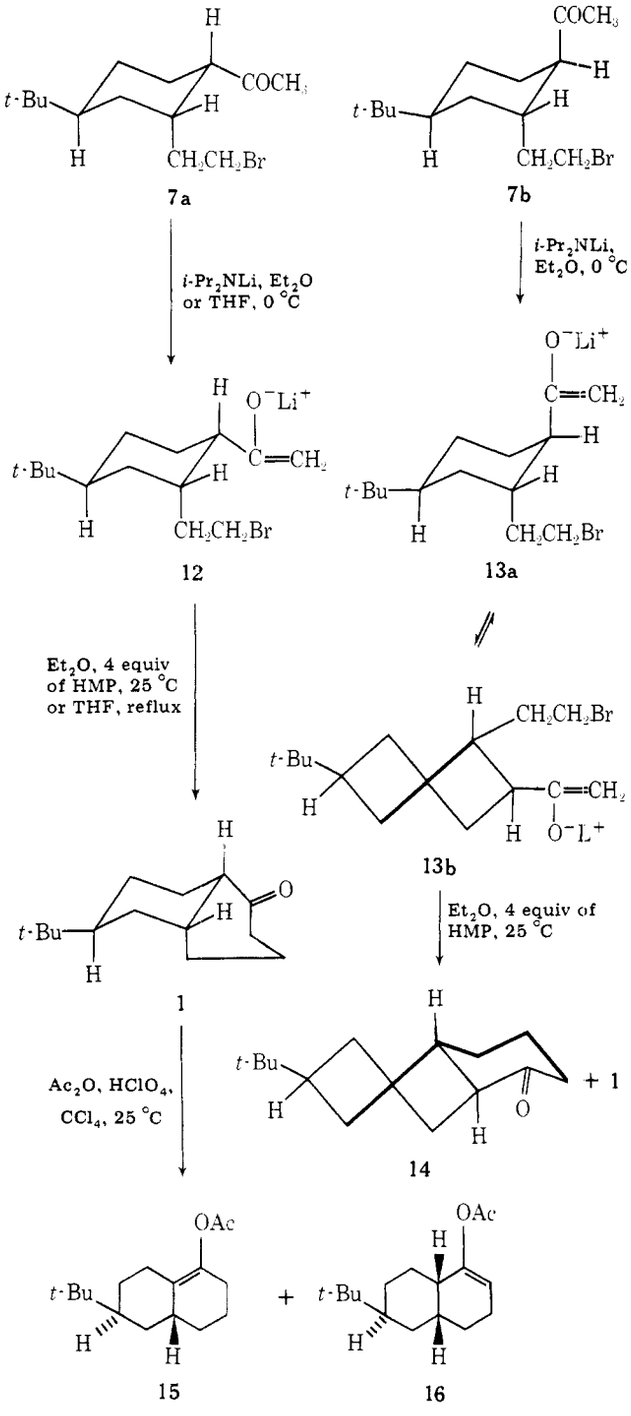
Scheme I



Since both epimers **5** have the appropriate stereochemical relationship between the *t*-Bu and CH_2=CH groups to be appropriate precursors for the desired decalone **1**, we examined the conversion of each epimeric olefin **5** to the corresponding bromo ketone **7** by the light-induced free-radical chain addition of HBr. In an earlier study[5a] of this HBr addition we noted a complication if this addition involved an olefin, $R_2CHCH{=}CH_2$, with a tertiary allylic CH bond. In such cases, including reactions with olefins **5** at 25 °C, the desired addition of a Br· radical to the double bond competes with abstraction of the allylic H atom by Br· to form an allylic radical such as **8**.[5a,6] Subsequent reaction of this allylic radical **8** with more HBr can either form a mixture of terminal olefins **5** and **6** or the structurally isomeric olefin **9**; free-radical chain addition of HBr to this olefin mixture **5**, **6**, and **9** then forms both the desired bromo ketones **7** and the unwanted isomers **10** and **11**. Thus, this competitive H-atom abstraction is clearly undesirable because it forms synthetic intermediates with either the wrong stereochemistry (**11**) or the wrong structure (**10**). Since free-radical addition reactions typically have a lower activation energy than free-radical atom abstraction reactions,[6,7] there was reason to expect that the importance of the competing H-atom abstraction reaction (to form **8**) could be diminished by lowering the reaction temperature.[6] In fact lowering the reaction temperature from 25 to 0 °C or less was sufficient to practically stop the competing reaction and allowed us to form a mixture of bromo ketones **7a** or **7b** from the vinyl ketone **5a** that was contaminated with <5% of the unwanted by-products **10** and **11**. Further purification by low-pressure liquid chromatography then allowed us to obtain pure samples of each desired bromo ketone epimer **7a** and **7b**.

Kinetic deprotonation of each of the bromo ketones **7a** and **7b** (Scheme II) with the hindered base *i*-Pr_2NLi as previously described[5b,c] allowed us to obtain the terminal enolates **12** and **13** needed for cyclization to the epimeric decalones **1** and **14**. Activation of the enolate **12**, either by addition of 4 molar equiv of $(Me_2N)_3PO$ (HMP) to an Et_2O solution at 25 °C[5b] or by refluxing a THF solution,[5c] resulted in cyclization to form the desired decalone **1** in 76–86% yield. This product was clearly different from the previously described[3] diastereoisomer **2**. Cyclization of the epimeric enolate **13** in refluxing THF yielded mainly the same decalone **1** indicating that the cyclization was accompanied by epimerization of the starting bromo ketone **7b** (→**7a**) and/or the initial product **14** (→**1**). However, when the cyclization was effected in Et_2O with 4 molar equiv of HMP, the major product was the trans-fused decalone **14** accompanied by lesser amounts of the cis-fused epimer **1**. Equilibration of these two decalone epimers with NaOMe in MeOH at 25 °C produced a mixture containing 6.5% **14** and 93.5% **1**. Thus, it is clear that the bromo enolate **13** is capable of cyclization, presumably via the twist boat

Scheme II



conformer **13b**, to form the trans-fused decalone **14**. If one considers the ΔG values for an axial CH_3CO group [1.17 kcal/mol,[8] a crude model for the enolate $C(OLi)=CH_2$] and an axial CH_3CH_2 group (1.75 kcal/mol,[8] a model for CH_2CH_2Br), the sum of these ΔG values (2.9 kcal/mol) is sufficiently close to the energy difference between chair and twist-boat cyclohexane rings (*ca.* 4 kcal/mol)[9] that appreciable concentrations of both conformers **13a** and **13b** would be expected. Thus, the successful cyclization **7b** → **14** is not an unreasonable result.

The usual[3] enol acetylation of the decalone **1** under equilibrating conditions (Ac_2O, $HClO_4$, CCl_4) produced a mixture of comparable amounts of enol acetates **15** and **16**. Since the stereoisomeric decalone **2** forms practically all more highly substituted enol acetate (analogous to **15**) under these same conditions, it seems likely that the octalin system represented by enol acetate **15** possesses a significant amount of conformational strain and may exist in a conformation with a twist-boat cyclohexane ring.[10] In any case, the methods described constitute an acceptable synthetic route to the decalone **1** and a suitable derivative **15** for the preparation of its lithium enolate. Our further studies of the alkylation stereochemistry of this enolate as well as the related question of the favored conformation of an enol derivative (e.g., **15**) are in progress and will be reported in a subsequent publication.

Experimental Section[11]

Separation of the Vinyl Ketones 5a and 5b. A 3.00-g sample of a crude product from reaction of the enone **4** with CH_2=$CHMgBr$ and Me_2SCuBr in THF[5a] [containing (GLC, silicone XE-60 on Chromosorb P) a derivative of the 1,2-adduct (retention time 5.2 min, ca. 6%), the ketone **6b** (14.0 min, ca. 0.3%), the ketone **5b** (18.3 min, ca. 34%), the ketone **6a** (20.6 min, ca. 5%), the enone **4** (22.6 min, ca. 3%), and the ketone **5a** (26.6 min, ca. 52%)] was chromatographed on a 2.5 × 100 cm column packed with Woelm silica gel (0.032–0.064 mm) and eluted with EtOAc–hexane (8:92 v/v). The early fractions contained 188 mg (6%) of liquid, $n^{25}D$ 1.4865, believed to be *p*-(*sec*-butyl)-*tert*-butylbenzene (formed from the 1,2-adduct by dehydration and C=C rearrangement). The spectral properties of the component were: IR (CCl_4), no OH or C=O absorption; NMR (CCl_4) δ 7.20 (2 H, d, J = 8 Hz, aryl CH), 7.00 (2 H, d, J = 8 Hz, aryl CH), 2.55 (1 H, sextet, J = 7 Hz, benzylic CH), 1.1–1.9 (11 H, m, aliphatic CH including a *t*-Bu singlet at 1.28), and 0.6–1.0 (6 H, m, two CH_3 groups); mass spectrum, *m/e* (rel intensity) 190 (M^+, 69), 176 (49), 175 (90), 173 (20), 162 (38), 161 (100), 146 (44), 131 (45), 91 (28), 57 (36), and 41 (19). Subsequent chromatographic fractions contained (GLC), in order of elution, 950 mg (32%) of relatively pure ketone **5b**, 288 mg (10%) of a mixture of ketones **5a** and **5b**, and 1.446 g (48%) of relatively pure ketone **5a**. Appropriate fractions were combined and rechromatographed to separate 798 mg (27%) of ketone **5b**, $n^{25}D$ 1.4730, that was further purified by short-path distillation to separate **5b** as a colorless liquid: mp 8.0–8.5 °C; $n^{25}D$ 1.4731; IR (CCl_4) 1712 (C=O), 1640 (C=C), and 921 cm^{-1} (CH=CH_2); mass spectrum, *m/e* (rel intensity) 208 (M^+, 0.7), 152 (40), 151 (17), 109 (62), 107 (16), 71 (19), 67 (17), 57 (81), 43 (100), and 41 (30); NMR (CCl_4) δ 4.8–6.3 (3 H, m, vinyl CH), 2.7–3.1 (1 H, m, allylic CH), 2.4–2.6 (1 H, m, COCH), 2.11 (3 H, s, $COCH_3$), 0.9–2.1 (7 H, m, aliphatic CH), and 0.81 (9 H, s, *t*-Bu). When the ^1H NMR spectrum of ketone **5b** was rerun at 100 mHz to examine the pattern attributable to the CHCO multiplet at δ 2.4–2.6, we obtained partial resolution into three closely spaced lines at 248, 250.5, and 253 Hz; the width at half-height of the envelope containing these peaks was 10 Hz. This observation is compatible with our assigned stereochemistry in which the COCH proton is equatorial and is coupled with two equatorial and one axial adjacent protons (typical J values all 2–3 Hz).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.90; H, 11.74.

Appropriate later fractions that were combined and rechromatographed afforded 1.17 g (39%) of pure (GLC) ketone **5a**, mp 24–25 °C, $n^{25}D$ 1.4728 (lit. $n^{25}D$ 1.4728,[4b] mp 17.5–18 °C[5a]), that was identified with a previously described[4b] sample by comparison of IR, NMR, and mass spectra.

Separation of the Vinyl Ketones 6a and 6b. Fractions from several reactions containing (GLC, silicone XE-60 on Chromosorb P) primarily the ketones **6b** (retention time 10.2 min) and **6a** (15.4 min) were combined and separated by preparative liquid chromatography on a column packed with silica gel and eluted with EtOAc–hexane (6:94 v/v). The early fractions contained (GLC) the ketone **6b** separated as a colorless liquid: IR (CCl_4) 1715 cm^{-1} (C=O); NMR (CCl_4) δ 5.6–6.2 (1 H, vinyl CH), 4.7–5.2 (2 H, m, vinyl CH), 2.77 (1 H, m, allylic CH), 1.0–2.3 (11 H, m, aliphatic CH including a CH_3CO singlet at 2.02), and 0.85 (9 H, s, *t*-Bu); mass spectrum *m/e* (rel intensity) 208 (M^+, 0.5), 152 (13), 109 (26), 71 (23), 58 (100), 57 (50), 43 (69), 42 (18), 41 (24), and 39 (14).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.81; H, 11.67.

Later chromatographic fractions contained (GLC) the ketone **6a** separated as a colorless liquid: IR (CCl_4) 1715 cm^{-1} (C=O); NMR (CCl_4) δ 4.8–6.1 (3 H, m, vinyl CH), and 0.8–2.6 (21 H, m, aliphatic CH including a CH_3CO singlet at 1.99 and a *t*-Bu singlet at 0.89); mass spectrum, *m/e* (rel intensity) 208 (M^+, 4), 151 (23), 109 (36), 107 (17), 67 (18), 57 (88), 43 (100), and 41 (32).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.74; H, 11.65.

The two ketones **6** were equilibrated to establish which epimer was more stable corresponding to the isomer **6a** with an equatorial acetyl

group. A solution of 21 mg of ketone **6b** and 21 mg of n-$C_{19}H_{40}$ (an internal standard) in 1 mL of MeOH and 1 mL of THF was treated with 5.5 μL (0.2 equiv) of methanolic 3.6 M NaOMe and stirred at 25.0 °C. Periodically aliquots of the solution were removed, quenched in an aqueous phosphate buffer (pH 7.0), extracted with hexane, dried, and analyzed (GLC, apparatus calibrated with known mixtures). An additional portion (0.3 equiv) of methanolic 3.6 M NaOMe was added after 5 h. After 140 h at 25 °C, the solution contained 1.3% of ketone **6b** and 98.7% of ketone **6a** (93% recovery of **6**). From a comparable experiment starting with the ketone **6a**, after 140 h at 25 °C the solution contained >98% of the ketone **6a** and <2% of the ketone **6b** (100% recovery of **6**).

Preparation of the Bromo Ketones 7. The previously described[5a] apparatus and reaction procedures were followed except that the photochemical reactor was cooled by circulating cold MeOH from an external, thermostated cooling system. The temperature of the circulating MeOH was monitored and kept at 0 to −1 °C at the outlet from the cooling jacket of the photochemical apparatus. In a typical experiment, a cold (0 °C or less) solution of 1.90 g (9.13 mmol) of unsaturated ketone **5a** in 350 mL of pentane was irradiated with ultraviolet light for 12 min while a stream of anhydrous HBr was passed through the solution. Then the solution was purged with N_2 (to remove excess HBr), washed with aqueous $Na_2S_2O_3$, dried, and concentrated to leave 2.25 g (85%) of crude bromo ketone **7** product as a colorless liquid that contained (NMR analysis) ca. 35% of **7b** and ca. 65% of **7a** but none of the secondary bromide **10** was detected. A 1.00-g aliquot of the product was chromatographed on Woelm silica gel with an EtOAc–hexane eluent (6:94 v/v) to separate 105 mg of earlier fractions containing (NMR analyses) the bromo ketone **7b** followed by 453 mg of fractions containing various mixtures of **7a** and **7b.** Subsequent fractions contained 410 mg of the bromo ketone **7a.** The intermediate fractions were rechromatographed on silica gel to separate 228 mg of **7b** (total yield 333 mg or 28%) and 208 mg of **7a** (total yield 618 mg or 53%). In another comparable hydrobromination of 1.50 g of the vinyl ketone **5a** for 10 min at −1 to 0 °C, chromatography separated 90 mg (ca. 4%) of early fractions containing (NMR) mixtures of dibrominated products and secondary bromide **10** followed by 1.74 g (84%) of fractions containing bromo ketones **7a** (ca. 65% of the mixture) and **7b** (ca. 35% of the mixture).

The ketone **7a** was obtained as a colorless liquid: n^{25}_D 1.4969; IR (CCl_4) 1710 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 3.15–3.5 (2 H, m, CH_2Br), 2.2–2.5 (1 H, m, CHCO), 1.0–2.1 (13 H, m, aliphatic CH including a CH_3CO singlet at 2.08), and 0.87 (9 H, s, t-Bu); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 209.8 (s), 54.3 (d), 40.8 (d), 33.7 (d), 32.1 (s), 31.9 (t), 29.8 (t), 29.3 (t), 28.3 (t), 27.3 (q, 3 C atoms), 26.2 (q), and 22.4 (t); mass spectrum, m/e (rel intensity) 290 (M^+, 0.05), 288 (M^+, 0.05), 208 (15), 193 (21), 151 (21), 123 (35), 110 (12), 109 (19), 95 (10), 81 (12), 57 (48), 43 (100), and 41 (27).

The ketone **7b** was obtained as a colorless liquid: n^{25}_D 1.4968; IR (CCl_4) 1710 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 3.37 (2 H, t, J = 7 Hz, CH_2Br), 1.0–2.6 (14 H, m, aliphatic CH including a CH_3CO singlet at 2.10), and 0.82 (9 H, s, t-Bu); mass spectrum, m/e (rel intensity) 290 (M^+, 0.5), 288 (M^+, 0.5), 209 (11), 153 (12), 123 (10), 109 (18), 95 (10), 81 (11), 71 (23), 57 (71), 55 (12), 43 (100), and 41 (29).

The most satisfactory analytical method for mixtures of the epimeric bromo ketones **7** utilized the ^1H NMR spectra. The ketone **7a** exhibited a t-Bu singlet at δ 0.87 with a complex multiplet (CH_2Br) centered at δ 3.33 while the ketone **7b** exhibited a t-Bu singlet at a higher field (δ 0.82) with a triplet (CH_2Br) at δ 3.37. The presence of the secondary bromide **10** in this mixture is readily detected by the presence of a t-Bu singlet at δ 0.89 and, especially, a CHBr multiplet at δ 4.22. When samples of either pure bromo ketone **7a** or **7b** (from chromatography) were distilled in a short path still (ca. 104 °C at 0.01 mm), mixtures of the two epimers were obtained. Thus, distillation of pure ketone **7a** afforded a colorless liquid, n^{25}_D 1.4970, that contained (NMR analysis) ca. 65% **7a** and ca. 35% **7b.**

Anal. Calcd for $C_{14}H_{25}BrO$: C, 58.12; H, 8.73; Br, 27.62. Found: C, 58.20; H, 8.72; Br, 27.49.

When an 835-mg sample of the epimeric vinyl ketone **5b** in 300 mL of pentane was subjected to the photoinitiated addition of HBr for 6 min at 25 °C, the resulting crude bromo ketone product amounted to 1.076 g. Chromatography on silica gel with an EtOAc–hexane eluent (8:92 v/v) separated in earlier fractions 44 mg of an unidentified crude dibrominated product as a colorless solid, mp 104.5–105.5 °C, followed by 18 mg (1.5%) of the crude secondary bromide **10** as a colorless liquid: NMR (CCl_4) δ 4.22 (1 H, q of d, J = 7 and 2 Hz, CHBr) and 0.8–2.4 [24 H, m, aliphatic CH including a CH_3CO singlet at 2.15, a CH_3 doublet (J = 7 Hz) at 1.65, and a t-Bu singlet at 0.89]. Later fractions contained 877 mg (76%) of mixtures of bromo ketones **7a** (ca. 64%) and **7b** (ca. 36%). The similar hydrobromination of 242 mg of vinyl ketone **5a** in 300 mL of pentane at 25 °C for 5 min afforded, after chromatography, 114 mg (ca. 32%) of a mixture of dibromo product and secondary bromo ketone **10** and 141 mg (42%) of fractions containing mixtures of bromo ketones **7a** and **7b.** Thus, it appears that the H-atom abstraction leading to by-products **10** and **11** is more serious at 25 °C with the vinyl ketone **5a** than with its epimer **5b.** The photoinitiated addition of HBr was repeated with a solution of 140.5 mg of the vinyl ketone **5b** in 310 mL of pentane at 0 °C for 6.5 min. After the crude product (183.6 mg) had been chromatographed, the fractions were subjected to the above NMR analysis. From the fraction weights and NMR analysis, the yields were estimated to be 28% bromo ketone **7b,** 52% bromo ketone **7a,** 3% secondary bromide **10,** and 3% dibrominated product.

Cyclization of Bromo Ketone 7a. A. In Et_2O Solution. Following a previously described[5b] procedure, a solution of 386 mg (1.33 mmol) of the bromo ketone **7a** in 10 mL of Et_2O was added, dropwise and with stirring during 30 min, to a cold (−78 °C) solution of 1.40 mmol of i-Pr_2NLi and 2 mg of 2,2′-bipyridyl (an indicator) in 2.7 mL of a pentane–hexane mixture and 20.6 mL of Et_2O. After the resulting solution of the enolate **12** (0.04 M) had been warmed to 0 °C, 1.00 g (5.58 mmol, 4 molar equiv per Li^+) of HMP was added and the solution was stirred at 0–2 °C for 20 min, allowed to warm to 23 °C during 20 min, and stirred at 23 °C for 40 min. The reaction mixture was partitioned between Et_2O and aqueous $NaHCO_3$ and the organic phase was dried and concentrated to leave 317 mg of crude product as a yellow liquid. An aliquot of the crude product was mixed with a known weight of n-$C_{20}H_{42}$ (an internal standard) for GLC analyses (silicone XE-60 on Chromosorb P, apparatus calibrated with known mixtures); the crude product contained several minor unidentified impurities (retention times 5.2, 6.9, 9.4, and 14.8 min), n-$C_{20}H_{42}$ (28.0 min), the *trans*-decalone **14** (34.6 min, 2.4% yield), and the *cis*-decalone **1** (41.5 min, 86% yield). A 275-mg aliquot of the crude product was chromatographed on Woelm silica gel with an EtOAc–hexane eluent (8:92 v/v) to separate 8.5 mg (3.5%) of an early fraction containing (NMR) the unchanged bromo ketone **7a** accompanied by small amounts of ketones **1** and **14.** Later fractions contained 184 mg (76%) of ketone **1** that was identified with the subsequently described sample by comparison of IR and NMR spectra and GLC retention times and shown to differ from the previously described[3] decalone diastereoisomer **2** by comparison of IR spectra.

B. In THF Solution. To a cold (−70 °C) solution of 8.11 mmol of i-Pr_2NLi and 4 mg of 2,2′-bipyridyl (an indicator) in 14.2 mL of a pentane–hexane mixture and 120 mL of THF was added, dropwise and with stirring during 45 min, a solution of 2.233 g (7.73 mmol) of the bromo ketone **7a** in 25 mL of THF. The resulting orange solution of the enolate **12** (0.05 M) was warmed to −20 °C during 10 min and then immersed in a preheated bath and refluxed for 45 min. After the reaction mixture had been subjected to the previously described isolation procedure, the crude product amounted to 1.60 g of red liquid. After an aliquot of the crude product had been mixed with n-$C_{20}H_{42}$, GLC analysis indicated the presence of ketone **1** (78% yield) and ketone **14** (9% yield). Distillation of the crude product separated 1.29 g (80%) of a mixture of ketones **1** (90% of mixture) and **14** (10% of mixture), bp 115–117 °C (0.35 mm), n^{25}_D 1.4865–1.4868, and left 0.22 g of a brown higher molecular weight residue. A 1.11-g aliquot of the distillate was chromatographed on Woelm silica gel to separate 83 mg (6%) of the *trans*-decalone **14** and 884 mg (64%) of the *cis*-decalone **1.** These latter fractions were distilled to separate 820 mg of the pure *cis*-decalone **1** as a colorless liquid: bp 81–82 °C (0.08 mm); n^{25}_D 1.4859; IR (CCl_4) 1709 cm^{-1} (C=O); UV_{max} (95% EtOH) 299 nm (ε 18); ^1H NMR (CCl_4) δ 0.9–2.4 (15 H, m, aliphatic CH) and 0.86 (9 H, s, t-Bu); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 214.5 (s), 53.1 (d), 41.2 (d), 37.5 (d and t, 2 C atoms), 32.0 (s), 31.4 (t), 27.2 (q, 3 C atoms), 26.8 (t), 25.8 (t), 25.7 (t), and 25.2 (t); mass spectrum, m/e (rel intensity) 208 (M^+, 13), 151 (22), 133 (30), 112 (22), 110 (34), 97 (98), 91 (32), 84 (28), 67 (34), 57 (100), 55 (25), and 41 (64).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.76; H, 11.64.

A collected (GLC) sample of the *trans*-decalone **14** was distilled in a short-path still to separate the ketone **14** as a colorless liquid: n^{25}_D 1.4853; IR (CCl_4) 1710 cm^{-1} (C=O, spectrum clearly different from the IR spectra of decalones **1** and **2**); NMR (CCl_4) δ 1.0–2.4 (15 H, m, aliphatic CH) and 0.90 [9 H, s, t-Bu (this signal is at 0.04 ppm lower field than the t-Bu signal at 0.86 for the *cis*-decalone **1**)]; mass spectrum, m/e (rel intensity) 208 (M^+, 12), 152 (24), 123 (20), 110 (35), 97 (21), 67 (22), 57 (100), 55 (24), 44 (24), and 41 (64).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found C, 80.89; H, 11.73.

In a larger scale preparation, 6.22 g (29.9 mmol) of a mixture of vinyl

ketones **5a** and **5b** (isolated by liquid chromatography) was subjected to light-catalyzed hydrobromination at 0 °C to yield, after column chromatography, 7.05 g (24.4 mmol, 82%) of a mixture of epimeric bromo ketones **7a** and **7b**. After a solution of this mixture in 30 mL of THF has been added to a cold (−78 °C) mixture of 400 mL of THF and 52.2 mL of a hexane–pentane solution containing 25.6 mmol of $(i\text{-Pr})_2$NLi, the resulting solution was refluxed for 75 min and then subjected to the usual isolation procedure. Chromatography of the crude product on silica gel separated 4.13 g (82% based on the bromo ketones 7 or 66% overall) of a mixture of decalones 1 and **14**.

Cyclization of the Bromo Ketone 7b. A. In Et_2O Solution. A solution of the enolate **13** (0.05 M) was prepared by the slow (40 min) addition of a solution of 475 mg (1.64 mmol) of the bromo ketone **7b** in 4 mL of Et_2O to a cold (−70 °C) solution of 1.73 mmol of $i\text{-Pr}_2$NLi and 2–3 mg of 2,2′-bipyridyl in 3.2 mL of a pentane–hexane mixture and 25 mL of Et_2O. After the orange enolate solution had been warmed to 0 °C, 1.24 g (6.92 mmol, 4 molar equiv per Li^+) of HMP was added and the mixture was stirred at 0–2 °C for 20 min, at 2–22 °C for 20 min, and the reflux (33 °C) for 20 min. After the reaction mixture had been partitioned between aqueous $NaHCO_3$ and Et_2O, the organic phase was dried, concentrated, taken up in pentane, washed with several portions of aqueous NaCl (to remove residual HMP), and again dried and concentrated. The residual red liquid (328 mg) contained (IR and NMR analysis) a mixture of the starting bromo ketone **7b** (no **7a** was detected) and the epimeric decalones **1** and **14**. Analysis by GLC (silicone XE-60 on Chromosorb P) indicated the presence of several relatively rapidly eluted components (retention times 6.5, 9.9, and 16.3 min) believed to be various enol ether isomers from decomposition of the bromo ketone **7b** in the GLC apparatus, the *trans*-decalone **14** (33.4 min, 17% of the decalone product), and the *cis*-discalone 1 (38.0 min, 83% of the decalone product). From a second comparable reaction (reaction time 20 min at 0–2 °C, 20 min at 0–25 °C, and 40 min at 25 °C) where an aliquot of the crude product was mixed with a weighed amount of $n\text{-C}_{20}\text{H}_{42}$, the calculated yield (GLC) was 44% of *cis*-decalone **1** and 12% of *trans*-decalone **14**.

A 205-mg aliquot of the crude product was chromatographed on Woelm silica gel with an Et_2O–hexane eluent (1:9 v/v) to separate 92 mg (45%) of early fractions containing (NMR analysis) the bromo ketone **7b** (ca. 58% of the mixture) and the *trans*-decalone **14** (ca. 42% of the mixture) and 22 mg (11%) of later fractions containing (NMR analysis) the bromo ketone **7a** (ca. 10% of the mixture) and the *cis*-decalone **1** (ca. 90% of the mixture). In addition, 48 mg of fractions containing various minor unidentified components and 33 mg (ca. 16%) of slowly eluted fractions containing higher molecular weight materials (presumably from intermolecular alkylation) were isolated. Based on fraction weights and NMR analysis, the calculated yields were 26% recovery of the bromo ketone **7b**, 1% of the bromo ketone **7a**, 19% of the *trans*-decalone **14**, and 10% of the *cis*-decalone **1**. Collected (GLC) samples of the *cis*-decalone **1** and the *trans*-decalone **14** were identified with previously described samples by comparison of IR spectra and GLC retention times.

B. In THF Solution. A solution of the enolate **13** (0.05 M) was obtained by the slow (15 min) addition of a solution of 310 mg (1.07 mmol) of the bromo ketone **7b** in 2.0 mL of THF to a cold (−60 °C) solution of 1.13 mmol of $i\text{-Pr}_2$NLi and 2 mg of 2,2′-bipyridyl in 2.1 mL of a pentane–hexane mixture and 16.8 mL of THF. The resulting yellow solution was stirred at −60 °C for 5 min and then immersed in a preheated bath and refluxed for 2 h. After the reaction mixture had been partitioned between Et_2O and aqueous $NaHCO_3$, the organic layer was dried and concentrated to leave 182 mg of crude red liquid product. A 175-mg aliquot was chromatographed on Woelm silica gel with an Et_2O–hexane eluent (9:91 v/v) to separate 4 mg of unidentified rapidly eluted material followed by 35 mg (16% yield) of the *trans*-decalone **14**, 95 mg (44% yield) of the *cis*-decalone **1**, and 37 mg (ca. 17% yield) of a mixture of higher molecular materials. Collected (GLC) samples of the decalones **1** and **14** were identified with previously described samples by comparison of IR spectra and GLC retention time.

Equilibration of Decalones 1 and 14. A solution of 31.2 mg (0.15 mmol) of the *trans*-decalone **14**, 15.4 mg of $n\text{-C}_{19}\text{H}_{40}$, and 0.03 mmol of NaOMe in 1.5 mL of MeOH and 1.5 mL of Et_2O was maintained at 25.0 °C. Aliquots (0.3 mL) were removed, diluted with 0.3 mL of Et_2O, and partitioned between hexane and an aqueous buffer (pH 7) at the following time intervals: 0.5, 8, 10, 13, and 31 h. The hexane phases were concentrated and analyzed by GLC (silicone XE-60 on Chromosorb P, apparatus calibrated with known mixtures); the retention times of the components were: $n\text{-C}_{19}\text{H}_{40}$, 16.0 min; *trans*-decalone **14**, 31.1 min; *cis*-decalone **1**, 36.3 min. The recovery of ketones **1** and **14** in the various aliquots ranged from 96 to 100% and the composition of the mixture became constant after 10 h at 6.5% *trans*-ketone **14** and 93.5% *cis*-ketone **1**. Comparable mixtures of **1** and **14** were obtained when the *cis*-ketone **1** was subjected to the same equilibrating conditions.

Preparation of the Enol Acetates 15 and 16. A solution of 312 mg (1.5 mmol) of the ketone **1** and 811 mg (7.9 mmol) of Ac_2O in 4.5 mL CCl_4 was treated with 0.025 mL of aqueous 70% $HClO_4$ and the resulting mixture was allowed to stand at 25 °C for 20 min. After the reaction mixture had been neutralized with aqueous $NaHCO_3$, it was partitioned between aqueous $NaHCO_3$ and an Et_2O–hexane mixture. The organic layer was dried, concentrated, and distilled at 1.0 mm in a short-path still to separate 330 mg (88%) of a mixture of enol acetates **15** and **16** as a pale yellow liquid. This material contained (GLC, silicone XE-60 on Chromosorb P, apparatus calibrated with known mixtures) 54% of the enol acetate **16** (retention time 51.8 min) and 46% of the enol acetate **15** (39.4 min) accompanied by less than 5% of the starting ketone **1** (44.2 min). This product was chromatographed on silica gel with an EtOAc–hexane eluent to separate early fractions containing 109 mg (29%) of the enol acetate **15** as a colorless liquid: n^{25}_D 1.4855; IR (CCl_4) 1752 (enol ester C=O) and 1704 cm^{-1} (weak, C=C); NMR (CCl_4) δ 1.0–2.4 (17 H, m, aliphatic CH including a CH_3CO singlet at 2.03) and 0.84 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 250 (M^+, 5), 208 (100), 151 (75), 149 (20), 133 (37), 123 (72), 110 (51), 91 (23), 57 (50), 55 (24), 43 (44), and 41 (39).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47; mol wt, 250.1933. Found: C,77.02; H, 10.72; mol wt. 250.1917.

Later chromatographic fractions contained 132 mg (35%) of the enol acetate **16** as a colorless liquid: n^{25}_D 1.4837; IR (CCl_4) 1758 (enol ester C=O) and 1690 cm^{-1} (C=C); NMR (CCl_4) δ 5.1–5.3 (1 H, m, vinyl CH), 1.0–2.5 (16 H, m, aliphatic CH including a CH_3CO singlet at 2.03), and 0.83 (9 H, s, *t*-Bu); mass spectrum, *m/e* (rel intensity) 250 (M^+, 6), 208 (96), 190 (26), 175 (20), 152 (29), 151 (83), 150 (27), 149 (26), 134 (64), 133 (100), 132 (22), 123 (24), 112 (24), 110 (29), 97 (90), 91 (61), 84 (53), 81 (23), 67 (36), 57 (85), 55 (40), 43 (72), and 41 (54).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47; mol wt, 250.1933. Found: C, 77.06; H, 10.70; mol wt, 250.1897.

Subsequent fractions from the chromatography contained 13.6 mg (4%) of the starting ketone **1**. In order to establish the presence of the cis-ring fusion in the enol acetate **16**, a solution of 39.6 g (0.16 mmol) of the enol acetate **16** and 0.9 mL of aqueous 1 M HCl in 2.4 mL of THF was stirred at 25 °C for 72 h. Aliquots of the solution were removed periodically and partitioned between Et_2O and aqueous $NaHCO_3$. Each organic layer was mixed with a known weight of $n\text{-C}_{19}\text{H}_{40}$ (an internal standard) for GLC analysis (silicone XE-60 on Chromosorb P, apparatus calibrated with known mixtures). The retention times for the various components were: $n\text{-C}_{19}\text{H}_{40}$, 22.9 min; enol acetate **15** and trans-fused ketone **14**, 37.9 min (not resolved); cis-fused ketone **1**, 47.8 min; enol acetate **16**, 55.2 min. As the hydrolysis proceeded the enol acetate **16** was slowly converted to the *cis*-ketone **1** accompanied by little if any (4% or less) of the *trans*-ketone **14** and the enol acetate **15**. After 72 h approximately 60% of the enol acetate **16** had been converted to the *cis*-ketone **1**. Collected (GLC) samples of these two products were identified with authentic samples by comparison of IR spectra and GLC retention times.

Registry No.—**1**, 67238-07-7; **4**, 37881-09-7; **5a**, 54678-11-4; **5b**, 54678-12-5; **6a**, 54678-13-6; **6b**, 54678-14-7; **7a**, 61675-07-8; **7b**, 61675-06-7; **10**, 61675-09-0; **12**, 67238-08-8; **13**, 67238-09-9; **14**, 67238-10-2; **15**, 67238-11-3; **16**, 67238-12-4; vinyl bromide, 593-60-2; *p*-(*sec*-butyl)-*tert*-butylbenzene, 25027-33-2.

References and Notes

(1) This research has been supported by Public Health Service Grant RO1-GM-20197 from the National Institute of General Medical Science. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.
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(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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Received February 14, 1978

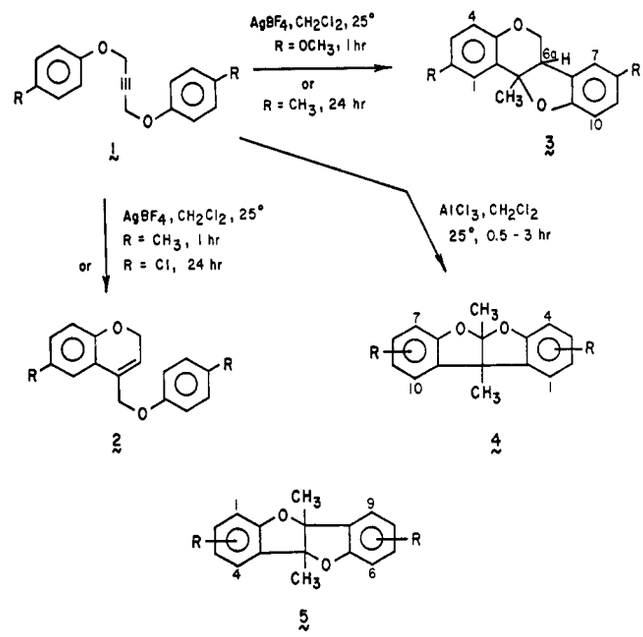
1,4-Bis(aryloxy)-2-butynes (1) can be selectively converted into 4-(aryloxymethyl)-2*H*-chromenes (2), 6*H*-benzofuro[3,2-*c*]-6a,11a-dihydro-11a-methylbenzopyrans (3), or 5a,10b-dihydro-5a,10b-dimethylbenzofuro[2,3-*b*]benzofurans (4) by treating a dichloromethane solution of 1 with mercuric trifluoroacetate, 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

0022-3263/78/1943-3856$01.00/0