The aromatic AA'BB' pattern, single *S*-methyl resonance, and a *C*-methyl signal in the overall ratio of 4:3:1 can fit only the symmetrical **2**. Condensation of *p*-methylthioacetophenone with two molecules of an aromatic seems an unexceptional reaction; however, it does not appear to have been reported.

In summary, the type and extent of sulfur complexation in thioanisole, and presumably analogous compounds, with Lewis acids can markedly affect the rate and product of some electrophilic reactions.

Experimental Section[7]

Materials. Reagents and solvents were used as obtained from commercial suppliers.

Pure ***p*-methylthioacetophenone** was obtained from an acetylation in EDC which was run equimolar in aluminum chloride, acetyl chloride, and thioanisole. The pure material showed mp 82–83°C (heptane) (lit.[8] 79–80°C); NMR (CCl_4) δ 2.45 (s, 6, CH_3), 7.45 (m, 4, aromatic). The two methyl groups were resolved by the addition of a little pyridine. Mass spectrum *m/e* (rel intensity) 166 (M^+, 59), 151 (100), 123 (21), 108 (14).

Pure ***o*-methylthioacetophenone** was formed by reaction of methyllithium with *o*-methylthiobenzoic acid in ether. Crystals from hexane showed mp 44.5–46.5°C (lit.[9] mp 45–47°C). The NMR was as previously described.[9] Mass spectrum *m/e* (rel intensity) 166 (M^+, 33), 151 (100), 127 (7), 108 (10). While this compound was readily separated from its para isomer on the GC column used,[10] resolution by TLC on commercial silica gel plates with hexane–benzene mixtures was unsatisfactory.

Acetylation Experiments. A. Entry 1, Table I. Two milliliters (28.1 mmol) of acetyl chloride was added over 2–3 min to a cold (−10 to −20°C) solution of 28.4 mmol of $AlCl_3$ and 30 mmol of thioanisole in 33 ml of EDC with stirring in a nitrogen atmosphere. The reaction mixture was warmed to and stirred at room temperature for 20–24 h, then quenched onto ice and water and worked up conventionally. The dried ($MgSO_4$) solution was diluted to a standard volume with EDC for quantitation by GC. Experiment 2 used 56 mmol of thioanisole and 30 ml of EDC; 3 used 141 mmol of thioanisole and 20 ml of EDC; and 4 was run with 311 mmol of thioanisole as reactant and solvent. All other aspects of these experiments were identical with 1 above.

B. Excess $AlCl_3$. Reaction was similar to A above, except that the mixture of 60.5 mmol of $AlCl_3$ and 30 mmol of thioanisole in 32 ml of EDC was a slurry at first. After addition of 28.1 mmol of acetyl chloride, substantial solution occurred. Work-up as before gave a product solution which represented a 98:2 para:ortho isomer ratio in 14% overall yield. Thin layer chromatograms of the nonvolatile constituents showed no other appreciable products.

C. To cold (−10 to −20°C) solutions of 28.1 mmol of acetyl chloride and 28.4 mmol of aluminum chloride in 27 and 32 ml of EDC were added 84.5 and 42.2 mmol of thioanisole, respectively. After completion and work-up as in A, the isomer ratios were 98.8:1.2 and 99.5:0.5, respectively.

D. Competitive Acetylation. To 4 g (30 mmol) of aluminum chloride in 18 ml of EDC were added 2.22 g (28.5 mmol) of benzene and 3.49 g (28.1 mmol) of thioanisole below 0°C. The $AlCl_3$ dissolved. A solution of electrophile was prepared by adding 2.21 g (28.2 mmol) of acetyl chloride to a cold (0 to −10°C) stirred slurry of 3.8 g (28.5 mmol) of aluminum chloride in 12 ml of EDC. The latter solution was added to the former below −10°C, and the reaction allowed to continue as with the others. After the same work-up GC determination showed 48.6:51.4 area ratios of *p*-methylthioacetophenone to acetophenone, equivalent to 43:57 molar ratios. The para/ortho ratio of methylthioacetophenones was 96:4.

By-Product Isolation. A reaction similar to entry 4 (Table I) was freed of most of the excess thioanisole by distillation under high vacuum following the normal work-up. The residue was crystallized from hot heptane to give impure methylthioacetophenone and a mother liquor enriched in the impurities. Fractional crystallization of the mother liquor residue first with ether, then ethyl acetate and acetonitrile gave the pure 1,3-diaryl-1-methylindene **1**, mp 145.5–146.5°C, needles from CH_3CN. The NMR is described in the text, as is the uv absorption spectrum. Mass spectrum *m/e* (rel intensity) 420 (M^+, 100), 405 (15), 373 (30), 166 (13), 151 (47), 149 (33).

Anal. Calcd for $C_{25}H_{24}S_3$: C, 71.38; H, 5.97. Found: C, 71.39; H, 5.95.

The other component, **2**, a triarylethane, was obtained from the above ether crystallization almost pure. Recrystallization twice from acetonitrile gave single spot material: mp 142–144°C; NMR ($CDCl_3$) δ 2.13 (s, 3, CCH_3), 2.44 (s, 9, SCH_3), 7.12 (q, 12, aromatic); mass spectrum *m/e* (rel intensity) 396 (M^+, 40), 381 (100), 366 (4.5), 287 (4.8), 273 (8.9), 272 (14), 178 (5.7), 174 (6.7).

Anal. Calcd for $C_{23}H_{24}S_3$: C, 69.65; H, 6.1. Found: C, 69.13; H, 5.79.

A portion of another experiment was chromatographed on preparative layer SiO_2 plates with hexane–benzene to give a fraction consisting almost exclusively of **1** and **2**. Integration of the ^1H NMR spectrum showed 11 and 15% conversions to **1** and **2**, respectively, from acetyl chloride.

Registry No.—**1**, 57559-89-4; **2**, 57559-90-7; *p*-methylthioacetophenone, 1778-09-2; aluminum chloride, 7446-70-0; acetyl chloride, 75-36-5; thioanisole, 100-68-5; *o*-methylthioacetophenone, 1441-97-0; *o*-methylthiobenzoic acid, 3724-10-5.

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(7) Melting points are uncorrected. Elemental analyses are by Mr. J. P. Gilbert and his associates of these laboratories, NMR spectra were obtained with a Jeolco C-60 HL or Hitachi Perkin-Elmer R-24A spectrometer. Mass spectra were obtained with an LKB 9000 spectrometer at 70 eV. For the sake of brevity, only portions of some spectra are reported.
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Regioselectivity in the Cyclization of β,γ-Epoxy Carbanions. Application to the Total Synthesis of *trans*-Chrysanthemic Acid[1]

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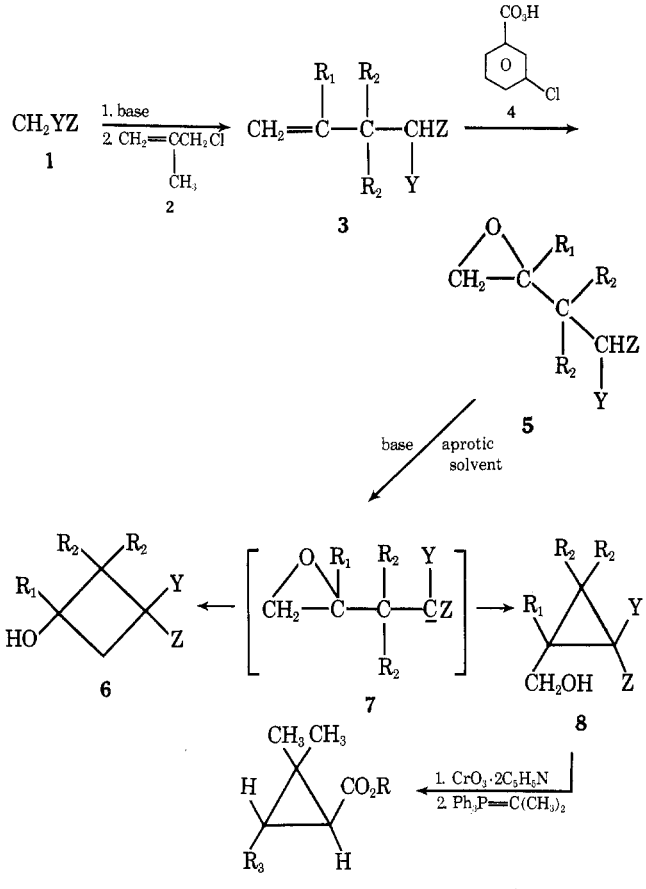
It is generally found that three- and five-membered carbocycles form considerably faster than four-membered rings in intramolecular displacement reactions.[2] A notable exception was recently reported[3] after a study of the regioselectivity in δ-epoxynitrile cyclizations involving SN2 type transition states. Such systems are unique in that, with equal substitution at both ends of the oxirane ring, cyclobutanes are always formed in preference to cyclopentanes. In view of the fact that previous reactions involving the base-promoted cyclization of the corresponding epoxy esters were generally carried out in protic solvents,[4] a study was undertaken to determine the site of attack in intramolecular alkylations undergone by β,γ- and γ,δ-epoxy carbanions in an aprotic solvent. The results of cyclizations undergone by a few representative β,γ-epoxy carbanions (**7**) are discussed in this note.

In two of the three systems (**5a,b**) examined, formation of a three-membered carbocycle requires substitution at a

tertiary carbon, whereas attack at the less hindered primary carbon would lead to a cyclobutanoid. In all systems examined, based on NMR and TLC analysis of the isolated reaction product, no evidence for formation of the four-membered carbocycle (**6**) was obtained.[5]

Epoxides **5a** and **5b** were prepared as outlined in Scheme I. Alkylation of diphenylmethane (**1a**) and ethyl phenylacetate (**1b**) with methallyl chloride (**2**) afforded the corresponding olefins (**3a,b**) in moderate yield. Subsequent treatment of the latter with *m*-chloroperbenzoic acid (**4**) afforded the corresponding epoxides (**5a,b**) in approximately 80% yield after purification via column chromatography. Base-promoted cyclization of these epoxides (**5a,b**) was achieved using anhydrous dimethyl sulfoxide as the solvent and sodium hydride to generate the intermediate anions (**7a,b**).

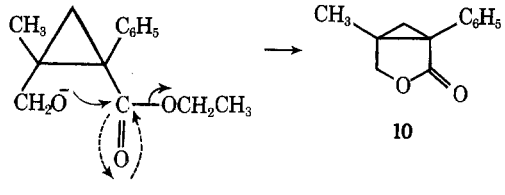
Scheme I



9d, R = CH_2CH_3; R_3 = CHO
e, R = CH_3; R_3 = CHO
f, R = H; $R_3 = (CH_3)_2C{=}CH$

a, R_2 = H; $R_1 = CH_3$; Y = Z = C_6H_5
b, R_2 = H; $R_1 = CH_3$; Y = C_6H_5; Z = $CO_2CH_2CH_3$
c, R_1 = Z = H; $R_2 = CH_3$; Y = $CO_2CH_2CH_3$

In one of the systems examined (**5b**), the only identifiable product after purification was a bicyclic lactone (**10**) whose formation from the intermediate cyclization product (**8b**) can be rationalized as shown below.



To illustrate the utility of this type of cyclization, a total synthesis of *trans*-chrysanthemic acid (**9f**),[6] many esters of which have insecticidal properties, has been achieved using the carbanion derived from an appropriately substituted epoxy ester (**5c**) as the key intermediate. The synthesis was effected as outlined in Scheme I. Ethyl 4,5-epoxy-3,3-dimethylpentanoate (**5c**) was prepared in 68% overall yield from 3-methyl-2-buten-1-ol[7] by a Claisen-type reaction[8] using triethyl orthoacetate, followed by epoxidation of the resulting unsaturated ester (**3c**) with *m*-chloroperbenzoic acid (**4**). Treatment of the resulting epoxy ester (**5c**) with 2 equiv of lithium diisopropylamide[9] and hexamethylphosphoramide in tetrahydrofuran at −70 °C afforded, after purification, only one identifiable product in 40% yield, cyclopropanoid **8c**. Since the sole isolated cyclization product obtained from epoxy ester **5b** was lactone **10** rather than the expected hydroxy ester **8b**, the absence of any lactone in the cyclization product obtained from epoxy ester **5c** indicates the trans stereochemistry of hydroxy ester **8c**. Further evidence was obtained by subsequent oxidation of the latter alcohol (**8c**) using chromium trioxide–pyridine complex in dichloromethane[10] to give in 90% yield the corresponding aldehyde (**9d**), whose NMR spectrum was compared to that previously reported[11] for methyl *trans*-2-formyl-3,3-dimethylcyclopropanecarboxylate (**9e**). Since the latter has been converted[11] to *trans*-chrysanthemic acid (**9f**), this step completes a formal total synthesis of this important terpenoid.

Experimental Section[12]

4,4-Diphenyl-2-methyl-1-butene (3a). Sodium metal (0.64 g, 27 mg-atoms) was added in small pieces to 60 ml of liquid ammonia to which had been added a small crystal of ferric nitrate. This mixture was stirred and refluxed (−33 °C) until the blue color had been discharged. After dropwise addition of a solution of 4.20 g (25 mmol) of diphenylmethane (**1a**) in 5 ml of anhydrous ether, the resulting deep red solution was stirred for an additional 30 min before 2.2 g (25 mmol) of methallyl chloride (**2**) in 5 ml of anhydrous ether was added dropwise over a period of 10 min. After the ammonia was allowed to evaporate slowly overnight, the mixture was partitioned between water and ether. Extraction with ether, followed by fractional distillation, afforded 2.38 g (43%) of olefin **3a**; bp 103–105 °C (0.40 mm) [lit.[13] bp 78–80 °C (0.01 mm)]; λ_{max} (film) 1655 (C=C), 1600, 1495, 890, 745, 695 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.33 (s, 10 aromatic H's), 4.75 (broad s, C=CH_2), 4.23 (t, J = 8 Hz, CH_2CH), 2.80 (d, J = 8 Hz, CH_2CH), 1.67 ppm (s, vinyl CH_3).

4,4-Diphenyl-2-methyl-1,2-epoxybutane (5a). A mixture of 2.22 g (10 mmol) of olefin **3a** and 2.10 g of 85% *m*-chloroperbenzoic acid (**4**)[7] in 50 ml of methylene chloride was refluxed for 15 h. After cooling this solution, it was washed twice with 1 M aqueous sodium hydroxide, and the crude product was isolated in the usual manner.[12] Chromatography on Florisil (elution with 5% ether–hexane) afforded 1.85 g (78%) of epoxide **5a**: λ_{max} (film) 1660, 1600, 1070, 1035, 810, 750, 705 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.35 (10 aromatic H's), 2.20 (s, CH_2O), 1.17 ppm (s, CH_3). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.41; H, 7.60.

(2,2-Diphenyl-1-methylcyclopropyl)methanol (8a). Epoxide **5a** (1.19 g, 5.0 mmol) in 10 ml of dimethyl sulfoxide was added dropwise over a period of 15 min to a vigorously stirred mixture of 6.0 mmol of sodium hydride in 40 ml of dimethyl sulfoxide. After this mixture was stirred at room temperature for 15 h, it was poured into 200 ml of H_2O and acidified with dilute hydrochloric acid, and the product was isolated by extraction with ether. Recrystallization of the crude product from 5% ether–hexane afforded 0.69 g (58%) of solid alcohol **8a**: mp 104–105 °C; λ_{max}(KBr) 3250 (OH), 1010, 770, 740, 695 cm^{-1}; δ_{Me_4Si}(CCl_4) 3.46 (s, CH_2OH), 1.57 (s, OH), 1.28 (AB quartet, peaks at 1.43, 1.35, 1.21, 1.13, 2 cyclopropyl H's), 1.11 ppm (s, CH_3). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.45; H, 7.77.

Ethyl 2-Phenyl-4-methyl-4-pentenoate (3b). A solution of 1.64 g (10 mmol) of ethyl phenylacetate (**1b**) in 10 ml of dimethyl sulfoxide was added dropwise to a vigorously stirred mixture of 12 mmol of sodium hydride in 50 ml of dimethyl sulfoxide. After evolution of hydrogen had ceased, a solution of 0.91 g (10 mmol) of methallyl chloride (**2**) in 10 ml of dimethyl sulfoxide was added

slowly. This mixture was subsequently stirred at room temperature for 2 h, after which it was diluted with 400 ml of water and the product was isolated by extraction with ether. Evaporative distillation afforded 1.34 g (62%) of unsaturated ester **3b:** bp 78–82 °C (bath temperature, 0.1 mm) [lit.[14] bp 136–138 °C (16 mm)]; λ_{max} (film) 1735 (C=O), 1650 (C=C), 1605, 1500, 1165, 1035, 900, 740, 700 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.41 (s, 5 aromatic H's), 4.82 (broad s, CH_2=C), 4.15 (quartet, J = 7 Hz, OCH_2CH_3), 1.73 (s, vinyl CH_3), 1.16 ppm (t, J = 7 Hz, OCH_2CH_3).

Ethyl 2-Phenyl-4-methyl-4,5-epoxypentanoate (5b). Using the procedure described above for the preparation of **5a,** epoxide **5b** was obtained in 74% yield as a colorless oil: λ_{max} (film) 1730 (C=O), 1160, 1030, 700 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.43 (s, 5 aromatic H's), 4.19 (quartet, J = 7 Hz, OCH_2CH_3), 1.28 (s, CH_3), 1.17 ppm (t, J = 7 Hz, OCH_2CH_3). Since this oily epoxide (**5b**) proved in our hands to be unstable to vacuum distillation, no attempt was made to further purify it.

1-Phenyl-2-oxo-5-methyl-3-oxabicyclo[3.1.0]hexane (10). Treatment of 0.600 g (2.56 mmol) of crude epoxide **5b** with 3.1 mmol of sodium hydride in 50 ml of anhydrous dimethyl sulfoxide using the procedure described above for the preparation of alcohol **8a** afforded, after chromatography on Florisil and recrystallization from 10% ether–hexane, 160 mg (34%) of bicyclic lactone **10:** mp 63–64 °C; λ_{max} (KBr) 1765 (C=O), 1165, 1075, 1010, 755, 695 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.54 (s, C_6H_5), 4.41 (AB quartet, peaks at 4.60, 4.45, 4.37, 4.22, CH_2O), 1.54 (AB quartet, peaks at 1.70, 1.62, 1.45, 1.37, 2 cyclopropyl H's), 1.09 ppm (s, CH_3). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.56; H, 6.43. Found: C, 76.65; H, 6.64.

Ethyl 3,3-Dimethyl-4-pentenoate (3c). A mixture of 1.718 g (19.94 mmol) of 3-methyl-2-buten-1-ol,[7] 26 ml of triethyl orthoacetate,[7] and 74 mg (1 mmol) of propionic acid was heated at 140° for 36 h under conditions that allowed distillative removal of ethanol through a Vigreux column. After cooling this solution, it was poured into 40 ml of 5% (v/v) aqueous sulfuric acid and this mixture was subsequently stirred (with cooling in a water bath to maintain the temperature at or below 25 °C) for 5 min to hydrolyze the excess triethyl orthoacetate. Extraction of the crude product with pentane, followed by chromatography on Florisil (elution with hexane–5% ether), afforded 2.204 g (71%) of ester **3c:** bp 35–45 °C (bath temperature, 0.10 mm); λ_{max} (film) 3120, 1735 (C=O), 1635 (C=C), 1230, 1200, 1120, 1025, 905 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.17–4.77 (complex pattern, 3 vinyl H's, peaks at 6.17, 5.99, 5.86, 5.69, 5.10, 5.08, 5.00, 4.97, 4.81, 4.79, and 4.77), 4.08 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.21 (s, CH_2C=O), 1.22 (triplet, J = 7.0 Hz, OCH_2CH_3), 1.13 ppm (s, CH_3CCH_3). Anal. Calcd for $C_9H_{16}O_2$: C, 69.21; H, 10.33. Found: C, 69.03; H, 10.29.

Ethyl 4,5-Epoxy-3,3-dimethylpentanoate (5c). A solution containing 1.214 g (7.78 mmol) of unsaturated ester **3c** and 10 mmol of *m*-chloroperbenzoic acid[7] in 20 ml of anhydrous ether was refluxed for 18 h. After washing the ether layer with 5% aqueous sodium hydroxide and saturated brine, epoxide **5c** was isolated in the usual manner[12] in 95% yield: bp 45–55 °C (bath temperature, 0.10 mm); λ_{max} (film) 1730 (C=O), 1260, 1230, 1115, 1030 cm^{-1}; δ_{Me_4Si} (CCl_4) 4.12 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.80 (triplet, J = 3.5 Hz, oxirane CH), 2.54 (d, J = 3.5 Hz, oxirane CH_2), 2.23 (s, CH_2C=O), 1.26 (t, J = 7.0 Hz, OCH_2CH_3), 1.0 (s, CH_3), 0.97 ppm (s, CH_3). Anal. Calcd for $C_9H_{16}O_3$: C, 62.78; H, 9.37. Found: C, 62.66; H, 9.36.

Ethyl 2-Hydroxymethyl-3,3-dimethylcyclopropanecarboxylate (8c). A solution of 944 mg (5.49 mmol) of ester **5c** and 2.0 ml of hexamethylphosphoramide in 10 ml of anhydrous tetrahydrofuran was added dropwise to a solution of 11 mmol of lithium diisopropylamide[9] in 50 ml of anhydrous tetrahydrofuran at −70 °C. After stirring this mixture at −70 °C for 7 h, the reaction was quenched by pouring the solution into 50 ml of saturated aqueous ammonium chloride solution. Extraction of the crude product with ether, followed by chromatography on Florisil (elution with 1:1 ether–hexane), afforded 378 mg (40%) of cyclopropanoid **8c:** bp 60–80 °C (bath temperature, 0.20 mm); λ_{max} (film) 3470 (OH), 1722 (C=O), 1205, 1170, 1110, 1025 cm^{-1}; δ_{Me_4Si} (CCl_4) 4.08 (quartet, J = 7 Hz, OCH_2CH_3), 3.57 (dd, variable broadening, CH_2OH), 1.25 (t, J = 7 Hz, OCH_2CH_3), 1.21 ppm (s, 2 CH_3's). Anal. Calcd for $C_9H_{16}O_3$: C, 62.78; H, 9.37. Found: C, 62.59; H, 9.47.

Ethyl *trans*-2-Formyl-3,3-dimethylcyclopropanecarboxylate (9d). Oxidation of alcohol **8c** was effected using the method developed by Ratcliffe and Rodehorst,[10] affording the corresponding aldehyde (**9d**) in 90% yield: bp 50–63 °C (bath temperature, 0.08 mm); >94% pure by VPC analysis,[15] oven temperature 155 °C, retention time 3.0 min; λ_{max} (film) 2775 (CHO), 1725 (ester C=O), 1700 (HC=O), 1225, 1170, 1100 cm^{-1}; δ_{Me_4Si} (CCl_4) 9.60 (d, J = 2.0 Hz, CHO), 4.12 (quartet, J = 7.0 Hz, OCH_2CH_3), 2.39 (d, J = 2.0 Hz, CHCHO), 2.37 (s, $CHCO_2CH_2CH_3$), 1.35 (s, CH_3), 1.30 (s, CH_3), 1.27 ppm (t, J = 7.0 Hz, OCH_2CH_3). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.23; H, 8.50.

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Registry No.—**1a,** 101-81-5; **1b,** 101-97-3; **1c,** 79-09-4; **2,** 563-47-3; **3a,** 33925-52-9; **3b,** 14815-83-9; **3c,** 7796-72-7; **5a,** 54949-91-6; **5b,** 57496-91-0; **5c,** 57496-92-1; **8a,** 27067-50-1; **8c,** 40427-26-7; **9d,** 38692-37-4; **9f,** 827-90-7; **15,** 57496-93-2; 3-methyl-2-buten-1-ol, 556-82-1.

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Efficient Syntheses of Barrelene and Nenitzescu's Hydrocarbon[1]

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Since their initial syntheses, the hydrocarbons barrelene (bicyclo[2.2.2]octa-2,5,7-triene, **1**)[2,3] and Nenitzescu's hydrocarbon (tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene, **2**)[4,5] have been of interest since they are of theoretical interest, themselves, and since they offered ready access to some $(CH)_8$ and $(CH)_{10}$ hydrocarbons, respectively.[6] The studies related to **1** and **2** have been hampered owing to the inaccessibility of sizable quantities of the hydrocarbons. For example, the syntheses of barrelene were accomplished in less than