Registry No. 1, 13066-51-8; 2, 41370-30-3; 3, 43052-87-5; 4a, 72445-15-9; 4b, 72445-16-0; 4c, 91112-21-9; 5, 78424-79-0; 6, 91112-18-4; 7, 78791-58-9; 8, 91112-23-1; 9, 91112-25-3; 10, 91112-26-4; 11, 91112-27-5; 12, 78424-72-3; 13, 78424-74-5; 14, 91112-19-5; 15, 57524-03-5; 16, 91112-20-8; prenyl chloride, 503-60-6.

An Intramolecular Acetylene Transfer between Anthracene and 5,6,7,8-Tetrafluorobenzobarrelene. A Novel Synthesis of Janusene and Dibenzobarrelene

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Janusene **3** has been constructed via the [4 + 2]-cycloaddition of dibenzobarrelene **2** to anthracene.[1] Until recently, dibenzobarrelene has been prepared in modest yields by various methods, including addition of acetylene to anthracene at elevated temperature and pressure.[2]

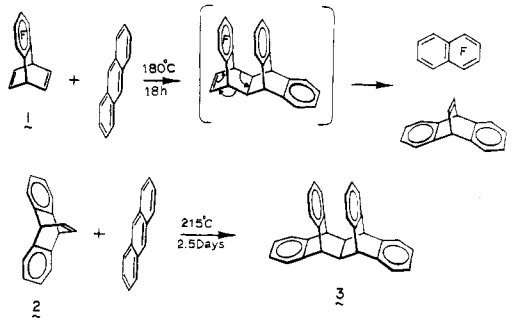
Disadvantages of direct addition of acetylene have stimulated the development of a number of acetylene equivalents.[3-5] The synthons thus far studied are dienophiles activated by electron-withdrawing groups which must be removed in a subsequent step. The conditions and reagents necessary for the removal of the activating moieties often limit the scope, result in undesirable byproducts, and reduce yields. The optimal acetylenic equivalent should consist of a dienophile which undergoes facile addition as well as subsequent regeneration of the olefinic group. Although phenyl vinyl sulfoxide meets both requirements, the byproduct is the undesirable phenylsulfenic acid.[3] The less reactive *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene obviates the latter problem but requires a two-step process[4] as does (*Z*)- and (*E*)-1,2-bis(phenylsulfonyl)ethylenes.[5]

We perceived that an efficient "one-pot" procedure could be accomplished by an addition–reversion sequence resulting in a relatively inert aromatic system. A precedent is the reaction of 5,6,7,8-tetrafluorobenzobarrelene and phenyl azide,[6] in which the monoadduct spontaneously cycloreverts to 1,2,3,4-tetrafluoronaphthalene and 1-phenyltriazole.

In this paper, we report the use of 5,6,7,8-tetrafluorobenzobarrelene (**1**) as the reactive acetylene transfer agent, with 1,2,3,4-tetrafluoronaphthalene as the latent leaving group to provide a vastly improved avenue to dibenzobarrelene and janusene (Scheme I).

In these reactions, readily available or easily prepared starting materials were employed. Unlike the laborious synthesis of barrelene[7] or benzobarrelene,[8] 5,6,7,8-tetrafluorobenzobarrelene was obtained directly from tetrafluorobenzyne and benzene,[9,10] in 48–55% yields.

Scheme I



Dibenzobarrelene was prepared in 91% yield by heating at 180 °C for 18 h an equimolar mixture of 5,6,7,8-tetrafluorobenzobarrelene and anthracene. The companion product 1,2,3,4-tetrafluoronaphthalene was isolated in 84% yield.

Janusene was obtained similarly, in 74% yield, by simply doubling the number of equivalents of anthracene relative to 5,6,7,8-tetrafluorobenzobarrelene and increasing the temperature to 215 °C, with a reaction period of 2.5 days.

Experimental Section

Melting points (uncorrected) were carried out on a Melt-Temp capillary apparatus. The infrared spectra in KBr were recorded on a Pye-Unicam 3-300 spectrophotometer. ^1H NMR spectra were determined at 60 MHz on a Varian T-60 spectrometer. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer at 20 MHz in $CDCl_3$. Chemical shifts were reported in parts per million relative to tetramethylsilane in solution.

Tetrafluorobenzyne was generated from pentafluorobenzene (PCR) and *n*-BuLi (2.5 M in hexanes) purchased from Aldrich. The anthracene was purchased from Eastman and used without further purification.

9,10-Dihydro-9,10-ethenoanthracene (Dibenzobarrelene). 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (274 mg, 1.21 mmol) (5,6,7,8-tetrafluorobenzobarrelene), prepared by the procedure of Callander,[10] was placed in a 1-mL ampule along with anthracene (210 mg, 1.18 mmol) and hydroquinone (10 mg). The ampule was sealed under dry N_2 and placed in a tube furnace. The reaction was conducted in a melt at 180 °C for 18 h. The resulting pale yellow glassy material was dissolved in dichloromethane, filtered through activated charcoal, and fractionally sublimed. 1,2,3,4-Tetrafluoronaphthalene (206 mg, 103 mmol, 84%) was recovered first (room temperature, 0.1 mmHg), followed by dibenzobarrelene[11] (225 mg, 1.09 mmol, 91%) (60 °C, 0.1 mmHg) [mp 117–118 °C (lit.[11] mp 118–119 °C)].

5,5a,6,11,11a,12-Hexahydro-5,12:6,11-di-*o*-benzenonaphthacene (Janusene). Janusene was prepared by placing 5,6,7,8-tetrafluorobenzobarrelene[10] (220 mg, 0.97 mmol), anthracene (345 mg, 1.90 mmol), and hydroquinone (15 mg) in a 1-mL ampule under purified N_2. The contents were heated in a tube furnace at 215 °C for a period of 2.5 days. The light brown

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glass was dissolved in dichloromethane and filtered through a small amount of activated charcoal. The dichloromethane was removed under reduced pressure and the remaining material fractionally sublimed. Sublimation gave 1,2,3,4-tetrafluoronaphthalene (152 mg, 0.76 mmol, 87%). Anthracene (44 mg, 0.25 mmol) and a trace of dibenzobarrelene were next recovered (60° C, 0.1 mmHg), and finally, pure janusene[12] (269 mg, 0.70 mmol, 74%) was collected (140 °C, 0.1 mmHg). ^{13}C NMR at 20 MHz not previously recorded: 145.6, 140.4, 125.6, 125.5, 125.3, 123.8, 49.1, 45.1 ppm.

Registry No. 1, 5162-34-5; 2, 2734-13-6; 3, 14707-22-3; anthracene, 120-12-7.

(12) Spectral and physical properties, including melting point (236–7 °C), were identical with those of an authentic sample of janusene graciously supplied to us by Prof. Stanley Cristol.

Epoxidation of 3-Cyclohexenemethanol. A Correction

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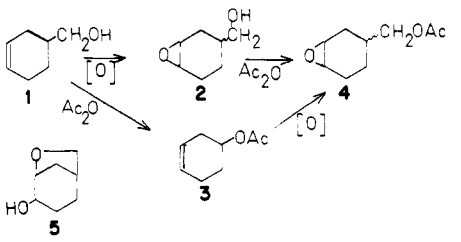
The presence of an alcohol or other hydrogen-bonding substituent in a position spatially proximate to a carbon–carbon double bond is well-known to accelerate the rate of epoxidation reactions and to strongly favor epoxidation from the side cis to the substituent.[1] These effects are evident in both peracid and catalyzed *tert*-butyl hydroperoxide (TBHP) reactions.[2] In the course of his pioneering experiments which elucidated this phenomenon, Henbest[3] reported that 3-cyclohexenemethanol (**1**) and its corresponding acetate (**3**) afforded predominantly the trans epoxides upon reaction with peracids. The evidence for this was chemical in nature. For accommodation of these results, the reacting conformations of **1** and **3** must be such that the side chain adopts a position capable of sterically shielding one side of the molecule without causing the mentioned cis epoxidation.

In the course of other work, we had occasion to examine the epoxidation of **1** and its derived acetate **3** using both MCPBA and TBHP. We can now report that, in both cases, epoxidation of **1** leads to a 1:1 mixture of cis and trans epoxy alcohols **2**. The evidence upon which this conclusion is based includes the ^{13}C NMR spectrum of the acetate **4** which, at 100 MHz, shows a doubling of seven of the nine absorptions and the 60-MHz ^1H NMR which shows two apparent doublets for the acetoxymethyl group. The acetate was chosen for the NMR experiments to increase the shift of the oxygenated methylene group and to eliminate any unusual conformational effects caused by intramolecular hydrogen bonding. The fact that exactly the same results are obtained from the epoxidation of acetate **3** as from epoxidation of alcohol **1** followed by acetylation using either MCPBA or TBHP insures that no rearrangement of **1** to the bicyclic alcohol **5** has occurred (Scheme I).[4]

Scheme I



For further analysis of the mixture, the 400-MHz ^1H NMR of **4** was obtained. As expected, the spectrum was quite complex in the δ 1.0–2.5 region, suggesting that geminally situated protons on the ring carbons have substantially different chemical shifts in many cases. The epoxide hydrogens occur as a broadened multiplet centered at δ 3.17. The acetoxymethyl group appears as two discrete signals of equal integrated intensity: a doublet (J = 6.1 Hz) at δ 3.85 and a doublet of doublets (J = 3.6 and 2.9 Hz) centered at δ 3.89. Decoupling studies confirm that the two absorptions arise from different spin systems since the signal at δ 3.89 was collapsed to a singlet by irradiation at δ 1.89 while the signal at δ 3.85 is unaffected. Inspection of molecular models does not suggest an obvious reason why only one diastereomer should possess nonequivalent protons. Nevertheless, these results confirm the formation of two diastereomers from the epoxidation of **1** or **3**.

Experimental Section

MCPBA Epoxidations of 1 and 3. In a typical experiment, 0.06 mol of 85% MCPBA was dissolved in 60 mL of methylene chloride and filtered. This solution was cooled in an ice-bath during the dropwise addition of 0.035 mol of 3-cyclohexenemethanol (**1**)[5] or its acetate (**3**).[6] The reaction mixture was stirred for 15 h at ambient temperature, filtered, and washed with aqueous sodium bicarbonate until the washings were basic. The dried ($MgSO_4$) solution was evaporated and distilled under reduced pressure to give pure epoxy alcohol **2** in 36% yield: bp 65–68 °C (0.15 mm).

Acetate **3** afforded epoxy acetate **4** in 95% yield: bp 135 °C (17 mm) (lit.[7] bp 119–120 °C (9 mm)). Acetylation of **2** using acetic anhydride in pyridine gave **4** which was identical with the product of epoxidation of **3**: ^{13}C NMR ($CDCl_3$) 171.1, 68.6, 68.4, 52.5, 52.4, 51.6, 51.1, 32.2, 29.4, 28.2, 27.1, 24.6, 23.7, 22.9, 21.1, 20.9; ^1H NMR ($CDCl_3$) (60 MHz) 3.85 (dd, 3 H, J = 3, 3Hz), 3.1 (m, 2 H), 0.5–2.5 (m, 10 H); (400 MHz) (CH_2O-protons) 3.85 (d, J = 6.1 Hz), 3.98 (dd, J = 3.6, 2.9 Hz).

Hydroperoxide Epoxidation of 1 and 3. In a typical procedure, 0.02 mol of alkene, 0.02 g of $Mo(CO)_6$, 0.02 g of Na_2HPO_4 were combined, dissolved in 20 mL of dichloroethane, and brought to reflux. Anhydrous TBHP–dichloroethane solution[2,8] (10 mL, 4.5 M) was added dropwise. The resulting solution was refluxed for 2 h. To the cooled solution was added 50 mL of 40% Na_2SO_3 solution and the mixture was stirred for 15 h at which time a negative starch–iodide test was obtained. The organic layer was separated and washed with water and brine. The dried solution was evaporated and the oil obtained was distilled to give pure epoxy acetate **4**[9] in 56% yield. This material was identical with that obtained from the peracid oxidation.

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(9) The epoxy alcohol **2** decomposed on distillation. ^1H NMR of the crude product confirms the presence of the expected product. In order to obtain a pure product, the acetate was made in situ by using acetic anhydride in pyridine.

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