Communications to the Editor

Facile Synthesis of Substituted Brendanes via Spirocyclopropane Participation

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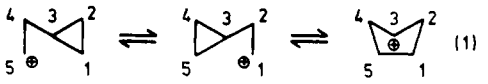
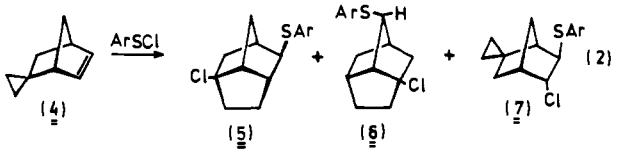
Ring expansion (**1** → **2**) and cyclopropane migration (**1** → **1a**)



(1)

(1a) (1) (2)

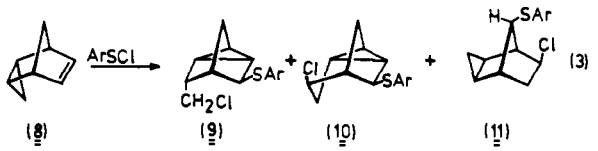
are possible structural transformations of β-cyclopropylethyl cations (**1**, eq 1). For the parent cation ring expansion has been documented as a significant pathway, but C-14 labeling rigorously excluded the cyclopropane migration route.[4] In the present communication we show that given the appropriate molecular skeleton, e.g., the norbornene moiety, spiroannelation as in **4**



(2)

(4) (5) (6) (7)

promotes ring expansion into the brendane derivatives **5** and **6** (eq 2), while endo fusion as in **8** involves cyclopropane migration (eq 3) during attack by *p*-toluenesulfenyl chloride.

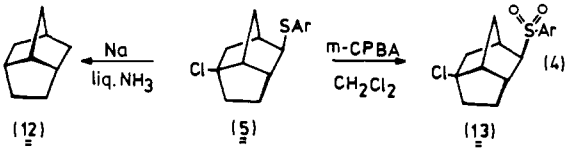


(3)

(8) (9) (10) (11)

Treatment of equimolar amounts of norbornene **4** and of *p*-toluenesulfenyl chloride in CH_2Cl_2 at 20 °C afforded a mixture of the three products **5**–**7**. These were separated by PTLC (SiO_2–petroleum ether), and analytical samples were obtained by means of Kugelrohr distillation.[5] The first fraction was the addition product **7** (ca. 10% yield), while the second and third fractions (15% and 26% yields, respectively), were identified as the brendane derivatives **6** and **5**.

Although the ^1H and ^{13}C NMR data were compatible with these structure assignments, in view of the unusual ring-expanding rearrangement involved in this electrophilic addition, rigorous chemical proof was needed. Indeed, either the mixture or pure samples of **5** and **6** were converted in over 90% yield to the parent brendane **12** on treatment with excess sodium in liquid ammonia (eq 4). The spectral data of **12** matched perfectly those reported for authentic brendane.[6] Furthermore, *m*-chloroperbenzoic acid

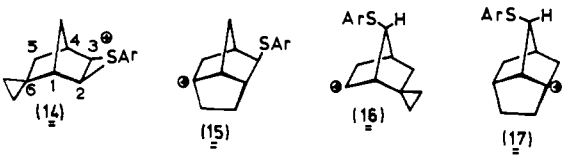


(4)

(12) (5) (13)

(*m*-CPBA) oxidation of **5** afforded the sulfone **13** (eq 4) in 81% yield as crystalline solid, whose structure was confirmed by X-ray analysis.

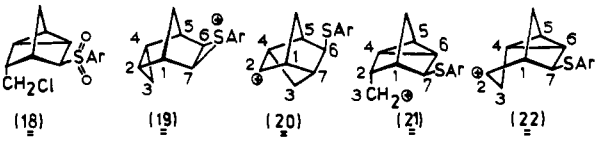
Electrophilic attack by the arenesulfenyl chloride on the double bond of norbornene **4** induces ring expansion of the spirocyclopropane moiety leading to the brendane derivative **5**. In view of the established three-center attack in the electrophilic addition of arenesulfenyl chlorides,[7] it is unlikely that free carbocationic intermediates as depicted in eq 1 intervene in this rearrangement. Instead, the initially formed cationic species is presumably the bridged episulfonium ion **14**. Even then, several features are



(14) (15) (16) (17)

remarkable about its subsequent ring expansion through spiropropane participation. First of all, regioselective attack of the chloride ion at the 3-position in cation **14** gives the electrophilic addition product **7**. Migration of the 1,6-bond produces the rearranged cation **16**. Such neighboring group participation has recently been convincingly demonstrated in norbornenes.[8] From a synthetic standpoint the fact that the β-cyclopropylethyl cations **14** and **16** undergo ring expansion to give the respective brendyl cations **15** and **17** is most interesting and valuable.

As an extension of this unusual ring-expansion process it was hoped that the norbornene **8** with an endo-fused cyclopropane ring would provide synthetic access into the brexane skeleton.[6] However, treatment of equimolar amounts of norbornene **8** with *p*-toluenesulfenyl chloride in CH_2Cl_2 at 20 °C gave a mixture of the three cyclopropane migrated products **9**–**11**. Chromatographic separation (PTLC (SiO_2–petroleum ether)) and final purification by Kugelrohr distillation provided analytical samples.[5] Tricyclooctane **10** (8% yield) eluted first, followed by the tricycloheptane **9** as the major product (29% yield). The latter was oxidized in 90% yield to the sulfone **18**, whose structure was rigorously established by X-ray analysis. The third fraction (5% yield) was identified as tricyclooctane **11**.



(18) (19) (20) (21) (22)

The desired ring expansion of the episulfonium ion **19** into the brexyl cation **20** did not take place. Instead, the cyclopropane ring migrated to C-6 either via 3,4- or 2,4-bond breaking to afford the rearranged β-cyclopropylethyl cations **21** and **22**, respectively, which are captured by chloride ion to give tricycloheptane **9** as major and tricyclooctane **10** as minor products. Of course, the free carbocations are intended here not as bona fide intermediates

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(2) N.C. thanks the Thyssen Stiftung for a travel grant.
(3) Max-Planck-Institut für Festkörperforschung.
(4) Cartier, G. E.; Bunce, S. C. *J. Am. Chem. Soc.* **1963**, *85*, 932.
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but rather as mechanistic constructs. The chemistry observed here for the episulfonium cation **19** matches perfectly that reported for the 3-nortricyclylcarbinyl cation.[9] The tricyclooctane **11** is the regular skeletal rearrangement product expected in arenesulfenyl chloride addition to norbornenes.[7,10]

Our results display an interesting mechanistic dichotomy about cyclopropylethyl cationic fragments that are embodied in the norbornyl skeleton. Thus, spiroannelated cyclopropanes as in norbornene **4** (eq 2) prefer ring expansion on arenesulfenyl chloride addition, thereby providing a facile and efficient entry into structurally complex molecules such as brendanes. Including the preparation of the norbornene **4**, the parent brendane **12** was prepared in three steps in an overall yield of 15% starting from cheap, commercial compounds. On the other hand, endo-fused cyclopropanes as in norbornene **8** prefer cyclopropane migration on arenesulfenyl chloride addition.

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Registry No. 4, 6572-50-5; **5**, 86146-93-2; **6**, 86146-94-3; **7**, 86146-95-4; **8**, 3635-94-7; **9**, 86146-96-5; **10**, 86146-97-6; **11**, 86162-06-3; **12**, 1521-75-1; **13**, 86146-98-7; **18**, 86146-99-8; *p*-toluenesulfenyl chloride, 933-00-6.

Supplementary Material Available: Experimental, physical, and X-ray data and structures of **13** and **18** (16 pages). Ordering information is given on any current masthead page.

(9) (a) Sauers, R. R.; Beisler, J. A.; Feilich, H. *J. Org. Chem.* **1967**, *32*, 569. (b) Wiberg, K. B.; Wenzinger, G. R. *Ibid.* **1965**, *30*, 2278.

(10) Of mechanistic interest is to mention that the exo-fused norbornene **8** gave exclusively 6-*endo*-chloro-7-*exo*-thio-*p*-tolueneoxytricyclo[3.2.1.$0^{2,4}$]-octane in 80% yield as the regular trans-addition product with arenesulfenyl chloride.

Proton-Transfer Spectroscopy of 3-Hydroxychromones. Extreme Sensitivity to Hydrogen-Bonding Perturbations[†,‡]

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The discovery of excited-state proton transfer in *o*-hydroxychromones[1] (structure I, R = phenyl in 3-hydroxyflavone and R = methyl in 2-methyl-3-hydroxychromone) has generated considerable interest in laser kinetic[2-4] and piezospectroscopic[5,6] study of the mechanism of the phototautomerization. Our extension of the original work now indicates that the presence of stoichiometric and substoichiometric traces of water, or other H-bonding impurities, in the supposedly dry hydrocarbon solvents controls and competes with the excited-state proton-transfer process.

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[‡]This work was presented at the Gordon Conference on Molecular Electronic Spectroscopy, Wolfeboro, NH, Aug 1982.

(1) Sengupta, P. K.; Kasha, M. *Chem. Phys. Lett.* **1979**, *68*, 382.
(2) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 6916.
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(5) Salaman, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1981**, *75*, 572.
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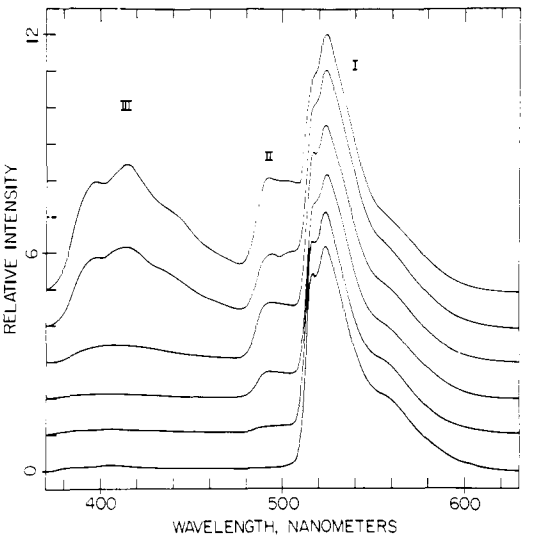
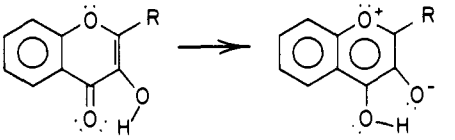
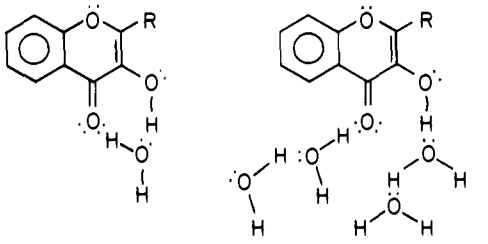


Figure 1. Fluorescence emission spectra of 2.00×10^{-5} M 3-hydroxyflavone in quick-frozen methylcyclohexane glass at 77 K as a function of addition of substoichiometric traces of water. Lowest curve shows unique tautomer fluorescence in the anhydrous solvent; highest curve, for a moderately wet solvent, shows tautomer fluorescence (I), perturbed-tautomer fluorescence (II), and "normal"-molecule fluorescence (III). The curves are normalized at 523 nm for clarity.

At temperatures greater than 200 K the roles of water solvates (structure II and III) are disguised, whereas at lower temperatures the properties of the solvated molecules dominate the excitation processes. In rigorously dry dilute hydrocarbon solutions, including both glass-forming and multicrystalline Shpol'skii matrices, we observe only the green tautomer fluorescence at all temperatures between 293 and 77 K.





The luminescence behavior at 77 K of 3-hydroxyflavone (2-phenyl-3-hydroxychromone) is reported in Figure 1. The solute concentration is 2.00×10^{-5} M in methylcyclohexane solvent. Because the effects that are to be described here are found to be strongly temperature and cooling-rate dependent, all spectra are reported for quick-frozen (i.e., sample tube plunged into liquid nitrogen) rigid-glass solutions at 77 K.

The lowest curve gives the luminescence spectrum of an extremely dry 3-hydroxyflavone solution.[7] The yellow-green fluoroescence is completely analogous to the room-temperature tautomer emission previously reported[1] and thus is associated with the unsolvated proton-transferred species (structure I, tautomer). Upon the addition of substoichiometric traces of water to the anhydrous hydrocarbon solution, a fluorescence shoulder, desig-

(7) For drying procedures refer to the full paper, ref 10.

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