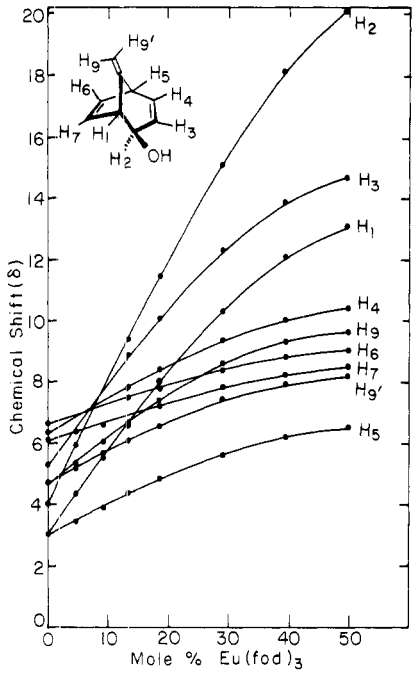
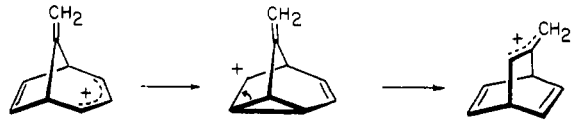


Figure 2. Plot of chemical shift vs. mol % $Eu(fod)_3$ for **4**.

carbon atoms and eliminates all tricyclic structures from consideration. It follows further that the dihydrobarrelene formulation is particularly consistent with the spectral features observed.

A mechanistic rationalization of the formation of **3–5** involves the assumption that **1** experiences initial ring opening to give symmetrical carbocation **6** which can either be captured by a nucleophile (with exo bonding favored by a factor of approximately 2) or experience further isomerization via **7** to **8**. The conversions of **6** to **7** and of **7** to **8** are straightforward homoallyl–cyclopropylcarbinyl rearrangements. While the driving force for conversion to **8** (or its capture by solvent) appears not to be overwhelming, it apparently derives in part from strain release.



6 **7** **8**

Experimental Section

Attempted Preparation of 1(5)-[(Methanesulfonyloxy)]-semibullvalene. Direct Conversion of 2 to 3–5. A mixture of 142 mg (1.06 mmol) of **2**,[5] 0.23 mL (1.65 mmol) of triethylamine, and 5.0 mL of dry ether under argon was cooled in a dry ice–carbon tetrachloride bath (–25 °C). To this solution was added dropwise 90 μL (1.20 mmol) of methanesulfonyl chloride over 2 min; a precipitate immediately started to form. After addition was completed, the cooling bath was allowed to warm gradually to room temperature over approximately 20 min. The reaction mixture, which now contained a large amount of precipitate, was added to a separatory funnel containing 50 mL of water and 25 mL of ether. The ether layer was washed with saturated sodium bicarbonate solution and brine and dried over sodium sulfate. Thin-layer chromatography on silica gel showed only one spot (R_f 0.38, 20% ether/carbon tetrachloride). Gas chromatographic analysis on a 6 ft × 0.25 in. 5% XF-1150 on 60/80-mesh Chromosorb W column (120 °C) showed two peaks: t_R 5.1 and 8.0 min, with relative areas of 48:52. These two components were separated to give 16 mg of the 5.1-min component, a solid, and 19 mg of **3**, a liquid. These samples were identified as $C_9H_{10}O$ isomers by their mass spectra: calcd m/e 134.0732, found 134.0733. Their ^1H NMR spectra and LIS studies [$Eu(fod)_3$] indicated that the 5.1-min component was a mixture of two compounds and that the 8.0-min component was pure. Resolution of the 5.1-min mixture into its components was accomplished on a 12 ft × 0.25 in. 15% FFAP on 60/80-mesh Chromosorb W column (120 °C): t_R 26.1 and 27.9 min, with relative areas of 61:39. Isolation of these two components gave 2.3 mg of **4** and 1.4 mg of **5**, respectively.

For **3**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.63 (dd, $J_{6,7}$ = 6.0, $J_{5,6}$ = 3.0 Hz, 1 H, H_6), 6.34 (ddd, $J_{3,4}$ = 9.5, $J_{4,5}$ = 6.0, $J_{2,4}$ = 1.7 Hz, 1 H, H_4), 5.89 (dd, $J_{6,7}$ = 6.0, $J_{1,7}$ = 3.0 Hz, 1 H, H_7), 5.22 (dm, $J_{3,4}$ = 9.5 Hz, 1 H, H_3), 4.67 (s, 1 H, H_9 or $H_{9'}$), 4.48 (s, 1 H, H_9 or $H_{9'}$), 4.32 (m, 1 H, H_2), 3.54 (m, 1 H, H_1), 2.93 (dd, $J_{4,5}$ = 6.0 Hz, $J_{5,6}$ = 3.0 Hz, 1 H, H_5), 2.02 (m, 1 H, hydroxyl).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.36; H, 7.48.

For **4**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.65 (dd, $J_{6,7}$ = 5.6, $J_{5,6}$ = 3.0 Hz, 1 H, H_6), 6.35 (dd, $J_{3,4}$ = 9.4, $J_{4,5}$ = 6.6 Hz, 1 H, H_4), 6.06 (dd, $J_{6,7}$ = 5.6, $J_{1,7}$ = 3.0 Hz, 1 H, H_7), 5.30 (ddd, $J_{3,4}$ = 9.4, $J_{2,3}$ = 3.4, $J_{1,3}$ = 1.9 Hz, 1 H, H_3), 4.70 (s, 1 H, H_9 or $H_{9'}$), 4.67 (s, 1 H, H_9 or $H_{9'}$), 4.20–3.94 (m, 1 H, H_2), 3.14–2.98 (m, 2 H, H_1 and H_5), 1.72 (br d, 1 H, $J_{2,OH}$ = 9.1 Hz).

For **5**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.72–6.16 (m, 4 H, H_1, H_2, H_3, and H_4), 4.94 (s, 1 H, H_9 or $H_{9'}$), 4.93 (s, 1 H, H_9 or $H_{9'}$), 4.16–3.74 (m, 3 H, H_5, H_6, and H_7), 1.35 (br d, $J_{6,OH}$ = 9.0 Hz).

Acknowledgment. We thank the National Science Foundation for their financial support of this work.

Registry No. **2**, 54007-60-2; **3**, 75600-62-3; **4**, 75600-63-4; **5**, 75600-64-5.

Cycloaddition Behavior of Heptalene toward Triazolinediones

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Received August 15, 1980

Although research in the area of heptalene chemistry lapsed seriously after Dauben and Bertelli's original synthesis of the nonbenzenoid hydrocarbon in 1961,[2] the last five years have witnessed a marked resurgence of interest in the field.[3] The principal underlying factor appears to be the successful development of efficient new synthetic routes both to the parent system[4,5] and to select stable derivatives[6–8] whose three-dimensional characteristics have been determined by X-ray methods.[9] Complementary

(1) (a) National Institutes of Health Postdoctoral Fellow, 1980–1981; (b) Ohio State University Graduate School Postdoctoral Fellow, 1976–1977.

(2) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 4659.

(3) Review: Paquette, L. A. *Isr. J. Chem.* **1980**, *20*, 233.

(4) (a) Vogel, E.; Königshofen, H.; Wassen, J.; Müllen, K.; Oth, J. F. M. *Agnew. Chem., Int. Ed. Engl.* **1974**, *13*, 732. (b) Vogel, E.; Kerimis, D.; Allison, N. T.; Zellerhoff, R.; Wassen, J. *Ibid.* **1979**, *18*, 545.

(5) (a) Paquette, L. A.; Browne, A. R.; Chamot, E. *Agnew. Chem., Int. Ed. Engl.* **1979**, *18*, 546. (b) Paquette, L. A.; Browne, A. R.; Chamot, E.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 643.

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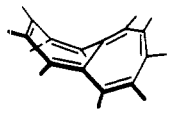
(8) Cycloheptatropolones and heptalenediones have also been prepared recently: (a) Kuroda, S.; Asao, T. *Tetrahedron Lett.* **1977**, *285*, 289; (b) Kato, K.; Oda, M; Kuroda, S.; Morita, N.; Asao, T. *Chem. Lett.* **1979**, 43.

(9) (a) Lindner, H. J.; Kitschke, B. *Agnew. Chem., Int. Ed. Engl.* **1976**, *15*, 106. (b) Stegemann, J.; Lindner, H. J. *Tetrahedron Lett.* **1977**, 2515.

0022-3263/80/1945-5381$01.00/0

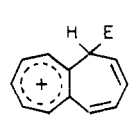
NMR studies have combined to establish that heptalene is not only nonplanar (see 1) but also capable of rapid ring inversion and π-bond shifting.[10]



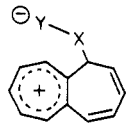
1

Heptalene is a bicyclic polyolefin which, because of its relatively high-lying HOMO, considers almost every reagent to be an electrophile and reacts with it as such. Treatment with $HSbCl_6$ precipitates 1-heptalenium hexachloroantimonate.[2] With other biparticulate[11] electrophiles such as iodine and nitronium hexafluoroantimonate, 1 provides products such as **2**.[12] Because these substances are very different to handle and purify, their characterization is founded on their spectroscopic properties alone.

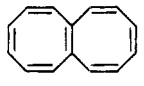
In view of this behavior, reaction of 1 with a biparticulate[11] electrophile (generalized here as X = Y) might be expected to proceed with initial bond formation as in **3**.



2
(E = I , NO_2)



3



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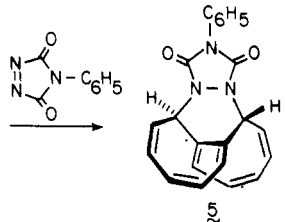
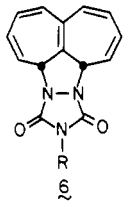
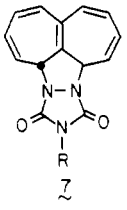


5

The site of the subsequent intramolecular capture of Y^- is not predictable a priori. Earlier, heptalene had been reported to afford polymeric material upon exposure to tetracyanoethylene.[12] In contrast, we have now found that 1 enters readily into cycloaddition with several triazolinediones. However, unlike the homologous octalene system (4) which furnishes the [8 + 2] adduct **5** where transannularly disposed carbon atoms of the two eight-membered rings have become bonded to nitrogen,[13] heptalene gives rise to a mixture of the epimeric adducts **6** and **7**.[14] Although these substances proved somewhat sensitive to chromatographic adsorbents, acids, and bases, they could be separated (with some loss) and shown to have the indicated molecular framework. Their monomeric nature was deduced by mass spectrometry and their inherent symmetry by ^{13}C NMR spectroscopy (seven signals arising from the carbocyclic portion). The more obvious features which distinguish the meso (80–90%) and *dl* (10–20%) isomers are the general downfield shift of the quaternary olefinic and allylic carbon signals of **6** relative to **7** and a corresponding upfield shift of the most deshielded olefinic protons in the ^1H NMR spectra. Their almost superimposable ultraviolet spectra [λ_{max} (C_2H_5OH) 250 nm (sh, ϵ 11 500–12 000)] compare closely to that exhibited by 1,10-dihydroheptalene.[2]

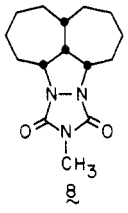


6



7

a, R = CH_3 ; b, R = C_6H_5 ; c, R =



8

In an initial attempt to distinguish between the C_2 and C_s forms of these adducts, heptalene was treated with (−)-*endo*-bornyltriazolinedione.[15] However, treatment of $CDCl_3$ solutions of the resulting **6c/7c** mixture with incremental amounts of tris[3-((trifluoromethyl)hydroxymethylene)-D-camphorato]europium(III) caused no alteration in the seven-line ^{13}C NMR patterns of the two carbocyclic moieties.

An appropriate means of distinguishing between **6** and **7** would be chemical modification of the central olefinic bond. Were functionalization to occur in cis fashion, the C_2 form (**7**) would suffer a loss of symmetry while the C_s form (**6**) would retain its meso status. This difference should be easily observed in the ^{13}C NMR spectra. Somewhat unexpectedly,[16,17] **6a** was slowly degraded by 3-chloro- and 3,5-dinitroperoxybenzoic acids[18,19] and by dichlorocarbene generated under phase-transfer conditions. Additionally, it proved totally inert to dichlorocarbene generated from sodium trichloroacetate, to diphenylisobenzofuran, and to ionic hydrogenation conditions.[20] Although this remarkable lack of reactivity also carries over to catalytic hydrogenation, **6a** could be completely reduced by the swamping catalyst technique (PtO_2, 52 psi, 6 days). The distinctive doublet of triplets resonance for the >CH–N< moiety of the perhydro adduct, which was obtained in two crystalline modifications, clearly identifies it to be **8**.

Having made this stereochemical distinction,[21] we conclude that the title cycloadditions are not concerted. The pair of adducts could be the result of competing exo and endo attack of the triazolinedione on heptalene (see 1) to

(10) (a) Vogel, E.; Wassen, J.; Königshofen, H.; Müllen, K.; Oth, J. F. M. *Agnew Chem., Int. Ed. Engl.* **1974**, *13*, 732. (b) Oth, J. F. M.; Müllen, K.; Königshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387.

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(12) Wilson, J. D. Ph.D. Thesis, University of Washington, 1966.

(13) (a) Vogel, E.; Runzheimer, H.-V.; Hogrefe, F.; Baasner, B.; Lex, J. *Agnew. Chem., Int. Ed. Engl.* **1977**, *16*, 871. (b) Oth, J. F. M.; Müllen, K.; Runzheimer, H.-V.; Mues, P.; Vogel, E. *Ibid.* **1977**, *16*, 872.

(14) Preliminary mention of these findings without stereoisomer designation was made in ref. 5a.

(15) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 3597.

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(17) Paquette, L. A.; Kretschmer, G. *J. Am. Chem. Soc.* **1979**, *101*, 4655.

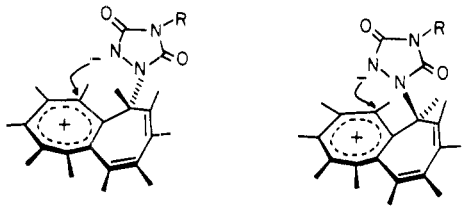
(18) Rastetter, W. H.; Richard, T. J.; Lewis, M. D. *J. Org. Chem.* **1978**, *43*, 3163.

(19) With the latter reagent, multiple products begin to appear at long reaction times. These have not been separated or identified.

(20) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

(21) We view the conversion of **6a** to **8** to be supportive, though not necessarily conclusive, evidence because of the possibility of double bond migrations during the long catalytic reduction procedure.

give **9** and **10** followed by rapid closure as indicated. Alternatively, the triazolinedione could be captured stereoselectively from the exo surface to give **9** which cyclizes at a sufficiently slow rate to allow conformational equilibration with **10** to intervene. It is the latter intermediate which serves as precursor to the major product; no interconversion of **6** and **7** has been observed.



9 **10**

Experimental Section

Addition of *N*-Methyltriazolinedione to Heptalene. To a solution of heptalene, prepared from 522 mg (3.34 mmol) of 1,6-dihydroheptalene,[5] in 90 mL of chloroform cooled to −78 °C was added dropwise a solution of *N*-methyltriazolinedione (376 mg, 3.33 mmol) in 25 mL of nitrogen-pruged chloroform. After completion of the addition, the magnetically stirred solution was maintained at room temperature for 1.5 h prior to concentration in vacuo. The residual solid was chromatographed on silica gel (elution with chloroform-ethyl acetate, 9:1) to give 420 mg (47%) of a mixture of **6a** and **7a** as a yellow foam. This material was subjected to preparative TLC on silica gel (elution with ethyl acetate–pentane, 1:1) to separate the isomers.

The high R_f major isomer (**6a**) was obtained as plates, mp 170.5–172.5 °C, after recrystallization from ethanol: IR (KBr) 3002, 1764, 1701, 1466, 1362, 1292, 1251, 1056, 982, 863, 803, 796 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.50–6.30 (m, 4 H), 6.15–5.78 (m, 2 H), 5.64–5.34 (m, 2 H), 4.50–4.35 (m, 2 H), 3.02 (s, 3 H); ^{13}C NMR ($CDCl_3$) 155.7, 136.4, 130.8, 129.8, 127.6, 124.9, 58.1, 25.6 ppm; *m/e* calcd 267.1008, obsd 267.1014.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.31; H, 5.01; N, 15.58.

The low R_f minor isomer (**7a**) was obtained as needles, mp 198–199 °C, from ethyl acetate–pentane: IR (KBr) 3000, 1765, 1710, 1460, 1387, 1240, 1035, 855, 790, 772, 757, 738, 695, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.78–6.59 (m, 4 H), 6.32–5.95 (m, 2 H), 5.60–5.30 (m, 2 H), 4.57–4.38 (m, 2 H), 3.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) 151.6, 131.5, 130.5, 124.8(2C), 123.9, 117.5, 56.6, 25.6 ppm; *m/e* calcd 267.1008, obsd 267.1014.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90. Found: C, 67.25; H, 4.91.

Addition of *N*-Phenyltriazolinedione to Heptalene. A solution of heptalene, as obtained from 800 mg (5.13 mmol) of the 1,6-dihydro derivative, was treated as above with 630 mg (3.59 mmol) of *N*-phenyltriazolinedione in 50 mL of chloroform. The residue obtained from column chromatography on silica gel (elution with chloroform-ethyl acetate, (1:1) was subjected to preparative TLC on silica gel (same eluent). The R_f 0.5 band was recrystallized from ethanol to give adduct **7b** as off-white microcrystalline needles: mp >310 °C dec; IR (KBr) 3010, 2910, 1770, 1710, 1600, 1505, 1433, 1423, 1272, 1234, 1138, 865, 752, 748, 694, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60–7.23 (m, 5 H), 6.78–6.03 (m, 6 H), 5.73–5.43 (m, 2 H), 4.67–4.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) 150.1 (s), 132.0 (s), 131.5 (d), 130.6 (d), 129.2 (d), 128.2 (d), 125.7 (d), 125.1 (s), 124.9 (d), 123.8 (d), 117.1 (s), 56.9 (d) ppm; *m/e* calcd 329.1164, obsd 329.1172.

Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.93; H, 4.59. Found: C, 72.82; H, 4.63.

The mother liquor from the first crystallization above was recrystallized twice more from ethanol and ethyl acetate–hexane. Each time a small amount of dirty brown sludge was removed. The remaining material was resubjected to TLC as above to finally give **6b** as an amorphous yellow solid: IR (KBr) 3015, 2920, 1770, 1710, 1600, 1503, 1413, 1127, 860, 755, 692, 6.15 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60–7.23 (m, 5 H), 6.62–5.80 (m, 6 H), 5.78–5.48 (m, 2 H), 4.72–4.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) 153.6 (s), 135.8 (s), 131.8 (s), 130.8 (d), 129.8 (d), 129.1 (d), 128.1 (d), 127.8 (s), 127.4 (d), 125.5 (d), 125.0 (d), 58.3 (d) ppm; *m/e* calcd 329.1164, obsd 329.1172.

Addition of (−)-*endo*-Bornyltriazolinedione to Heptalene. A solution of the optically pure triazolinedione in chloroform was added to a solution of heptalene in chloroform in the predescribed manner. The semisolid (80:20 mixture) obtained from preparative TLC was recrystallized twice from ethanol to give major isomer **6c** as pale yellow needles: mp 200–202 °C; IR (KBr) 3025, 2960, 2940, 2475, 1770, 1718, 1420, 1394, 1386, 1308, 1093, 870, 765, 759, 742, 696, 624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.57–5.87 (m, 6 H), 5.73–5.43 (m, 2 H), 4.57–4.40 (m, 2 H), 4.40–4.10 (m, 1 H), 2.67–2.27 (m, 1 H), 1.97–1.50 (m, 6 H), 1.00 (s, 3 H), 0.93 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) 156.8, 136.3, 131.5, 130.9, 130.5, 129.8, 127.7, 124.8, 59.4, 58.4, 51.6, 47.8, 45.5, 29.6, 27.1, 26.3, 19.7, 18.8, 14.0 ppm; *m/e* calcd 389.2103, obsd 289.2109.

Anal. Calcd for $C_{24}H_{27}N_3O_2$: C, 74.01; H, 6.99. Found: C, 73.69; H, 7.08.

No attempt was made to purify the minor isomer.

Catalytic Hydrogenation of 6a. A solution of **6a** (117.5 mg, 0.44 mmol) in ethyl acetate containing platinum oxide (102 mg) was hydrogenated in a Parr apparatus at 52 psi for 26 h. At this time, an additional 107 mg of PtO_2 was added and the hydrogenation was continued. Two more portions of PtO_2 (96.6 and 112 mg) were also added over the next 3 days. After a total reaction time of 6 days, the catalyst was separated by filtration through Celite and the filtrate was concentrated. The residual colorless solid was recrystallized from ethyl acetate–hexane and then hexane to give 48.7 mg (40%) of **8** as white needles, mp 122.5–123.5 °C. Very slow recrystallization from hexane at room temperature led to the appearance of a second crystalline form of **8**: thin plates; mp 134.5–135 °C; IR (KBr) 2910, 2900, 2839, 1765, 1710, 1465, 1450, 1395, 1380, 1200, 1175, 1160, 1030, 1020, 930, 765, 760, 735, 685, 640, 588 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.25–4.0 (d of t, J = 9, 6 Hz, 2 H), 3.13–2.87 (m with superimposed s, 4 H), 2.34–1.15 (series of m, 17 H); ^{13}C NMR ($CDCl_3$) 154.4, 60.9, 53.8, 40.4, 33.7, 30.3, 28.3, 25.1, 23.9 ppm; *m/e* calcd 277.1790, obsd 277.1799.

Anal. Calcd for $C_{15}H_{23}N_3O_2$: C, 64.95; H, 8.36; N, 15.15. Found: C, 64.89; H, 8.38; N, 14.96.

Acknowledgment. We thank the National Science Foundation (Grant CHE-7900333) for their partial financial support of this research.

Registry No. 6a, 75600-13-4; **6b**, 70528-33-5; **6c**, 75600-14-5; **7a**, 75600-15-6; **7b**, 70528-32-4; **8**, 75600-16-7; heptalene, 257-24-9; *N*-methyltriazolinedione, 13274-43-6; *N*-phenyltriazolinedione, 4233-33-4; (−)-*endo*-bornyltriazolinedione, 73462-83-6.

Bursatellin: A New Diol Dinitrile from the Sea Hare *Bursatella leachii pleii*

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Received August 1, 1980

Sea hares have yielded a fascinating array of natural products, most of which appear to be accumulated from diverse dietary sources.[1] Interest in the chemistry of these opisthobranch molluscs has been stimulated by the reputed toxicity of some species,[1,2] the observation of cytotoxic activity in sea hare extracts,[3,4] and the promise of

(1) P. J. Scheuer, *Isr. J. Chem.*, **16**, 52 (1977).
(2) B. W. Halstead, "Poisonous and Venomous Marine Animals of the World", Vol. 1–3, U. S. Government Printing Office, Washington, D. C., 1965, 1967, 1970.
(3) F. J. Schmitz, D. P. Michaud, and K. H. Hollenbeak, *J. Org. Chem.*, **45**, 1525 (1980), and references cited therein.

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