Communications

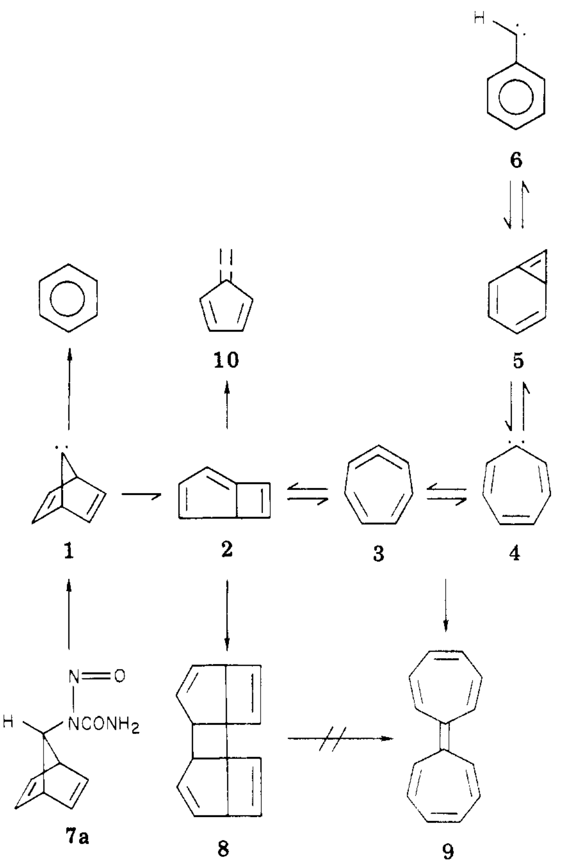
7-Norbornadienylidene: A New Member of the C_7H_6 Energy Surface

Summary: 7-Norbornadienylidene, generated by pyrolysis of the corresponding N-nitrosourea, competitively loses carbon to give benzene and rearranges to bicyclo[3.2.0]-heptatriene which either dimerizes, opens to cycloheptatrienylidene–cycloheptatetraene, or rearranges to fulveneallene.

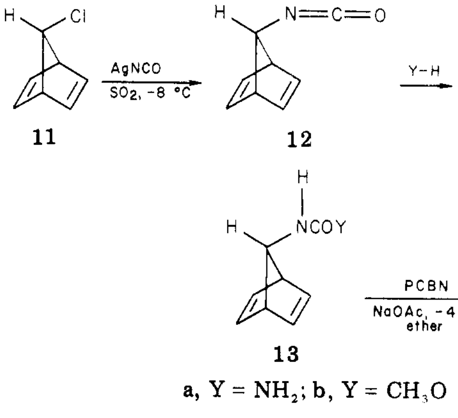
Sir: The number of high-energy C_7H_6 isomers continues to grow and their interrelationship appears to be gradually crystallizing. Thus, the interconversion of phenylcarbene, bicyclo[3.1.0]heptatriene (**5**) and cycloheptatrienylidene (**4**) is relatively secure.[1,2] Furthermore, evidence for cycloheptatetraene (**3**) in equilibrium with cycloheptatrienylidene is beginning to accumulate[2] and bicyclo[3.2.0]heptatriene (**2**), which was generated some years ago[4] (and its cis and trans dimers **8** characterized[4,5]), has very recently been proposed[6] as an intermediate in conversion of phenylcarbene (via cycloheptatrienylidene) to vinylidenecyclopentadiene(fulveneallene, **10**) (Scheme I). Finally, methylenecyclohexadienylidene and 1,2,4,5-cycloheptatetraene have been postulated as C_7H_6 intermediates from pyrolysis of benzocyclopropene[1b] and 1,2-diethynylcyclopropane,[3] respectively. However one member of the high-energy C_7H_6 family that has eluded prior generation attempts is 7-norbornadienylidene (**1**), an isomer that is of special interest because it is the premier example of the so-called foiled carbenes.[7] At this time we report evidence for the generation of **1**, an intermediate that rearranges to **2** which, in turn, can either dimerize to **8**, open to **10**, or cross into the cycloheptatrienylidene–cycloheptatetraene manifold.

Of the three methods that have been traditionally used to generate carbenes under relatively mild conditions,[8] neither the Bamford–Stevens reaction nor the base induced α elimination of HX have shown any promise for generation of **1**. In the former case, attempts to indirectly prepare the tosylhydrazone of 7-norbornadienone failed.[9] In the latter, strong base has been reported to substitute for halogen rather than effect elimination.[10] We therefore undertook an exploration of the third method, thermal or base-induced decomposition of *N*-nitrosamide derivatives.[11]

Scheme I



Scheme II



a, Y = NH_2; b, Y = CH_3O

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(1) Cf. (a) W. M. Jones and U. H. Brinker in "Percyclic Reactions", A. P. Marchand and R. E. Lehr, Ed., Academic Press, New York, N.Y., 1977; (b) C. Wentrup, *Top. Curr. Chem.*, **62**, 175 (1976).

(2) W. M. Jones, *Acc. Chem. Res.*, **10**, 353 (1977); C. Mayor and W. M. Jones, *J. Org. Chem.*, **43**, 4498 (1978).

(3) R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973).

(4) R. Breslow, W. Washburn, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969); R. Breslow and W. Washburn, *ibid.*, **92**, 427 (1970).

(5) N. L. Bauld, C. E. Dahl, and Y. S. Rein, *J. Am. Chem. Soc.*, **91**, 2787 (1969).

(6) C. Wentrup, E. Wentrup-Byrne, and P. Müller, *J. Chem. Soc., Chem. Commun.*, 210 (1977).

(7) (a) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968); (b) L. Skattebol, *Tetrahedron*, **23**, 1107 (1967); (c) M. H. Fisch and H. D. Pierce, *Chem. Commun.*, 503 (1970); (d) P. K. Freeman, R. S. Raghavan, and D. G. Kuper, *J. Am. Chem. Soc.*, **93**, 5288 (1971); (e) G. W. Klumpp and J. J. Frielink, *Tetrahedron Lett.*, 539 (1972); (f) H. Shechter et al., *J. Am. Chem. Soc.*, **94**, 5366 (1972); (g) M. S. Baird and C. B. Reese, *J. Chem. Soc., Chem. Commun.*, 523 (1972); (h) G. N. Fickes and C. B. Rose, *J. Org. Chem.*, **37**, 2898 (1972); (i) S. I. Murahashi, K. Okumura, T. Kubota, and I. Moritani, *Tetrahedron Lett.*, 4197 (1973); (j) S. I. Murahashi, K. Okumura, Y. Maeda, A. Sonada, and I. Moritani, *Bull. Chem. Soc. Jpn.*, **47**, 2420 (1974); (k) J. R. Neff and J. E. Nordlander, *J. Org. Chem.*, **41**, 2590 (1976); (l) R. A. Moss, U. H. Dolling, and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971); (m) R. A. Moss and V. H. Dollings, *ibid.*, 5117 (1972); (n) R. A. Moss and C. T. Ho, *ibid.*, 1651 (1976); (o) *ibid.*, 3397 (1976).

(8) Cf. W. Kirmse, "Carbene Chemistry", 2nd Ed, Academic Press, New York, N.Y., 1971.

(9) J. M. Landesberg and J. Sieczkowski, *J. Am. Chem. Soc.*, **93**, 972 (1971); T. Ledford, unpublished work.

(10) S. I. Murahashi, K. Hino, Y. Maeda, and I. Moritani, *Tetrahedron Lett.*, 3005 (1973).

(11) Cf. (a) D. L. Muck and W. M. Jones, *J. Am. Chem. Soc.*, **88**, 74 (1966); *ibid.*, **88**, 3798 (1966).

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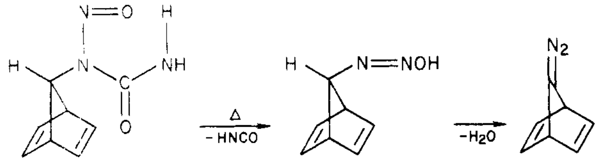
N-Nitroso-*N*-(7-norbornadienyl)urea and the corresponding methyl carbamate (**7a,b**) were prepared as depicted in Scheme II.[12] Nitrosation was the most difficult step in this scheme because most of the standard nitrosating agents[13] (sodium nitrite, N_2O_4, NOCl) apparently react too rapidly with the double bonds. However, *p*-chlorobenzoyl nitrite[14] (PCBN) gave the desired *N*-nitroso products in satisfactory yields.

Attempts to generate **1** by reaction of either **7a** or **7b** with base failed. Under no conditions were any products that could reasonably be attributed to 7-norbornadienylidene observed. We therefore turned our attention to a relatively obscure method to generate diazoalkanes from *N*-nitrosoureas: pyrolysis.[11,15] The probable mechanism of this reaction,[11] as applied to the 7-norbornadienyl system, is given in eq 1.



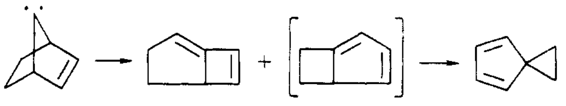
(1)

Pyrolysis of **7a** at 90 °C in heptane gave, among a number of unidentified products, 7-norbornadienyl isocyanate. By analogy with the thermal decomposition of *N*-methyl-*N*-nitrosourea,[15] this probably signals formation of 7-diazonorbornadiene.

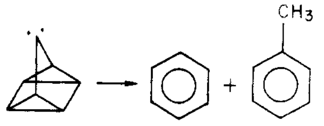
$$CH_3N(NO)CONH_2 \xrightarrow[-H_2O]{\Delta} CH_2N_2 + HNCO \rightarrow CH_3NCO$$

Unfortunately attempts to avoid the undesired side reaction with HNCO failed. We therefore turned to the gas phase. Pyrolyses were carried out by dropping crystalline **7a** onto the hot surface of an inclined flash vacuum pyrolysis tube[16] as previously described.[17] Volatile products were collected in a trap cooled with liquid nitrogen. A glass wool plug at the entry satisfactorily broke aerosols. In all pyrolyses, a colorless liquid was formed that solidified to cyanuric acid upon warming. Water, the other expected condensable inorganic product, was also invariably observed. Quantitative results were generally of poor reproducibility (e.g., yield of **8** at 250 °C varied from 14 to 34%). However, qualitative trends are clear. At 200 °C, a mixture of dimers **8**[18] was formed along with benzene. No heptafulvalene appeared at this temperature. As the temperature was raised, heptafulvalene[18,19] appeared, peaking at about 350 °C. Above 300 °C, dimers **8** were no longer observed and above 350 °C, heptafulvalene disappeared. At 400 °C a small amount of fulveneallene was detected (as its TCNE adduct).[21] At all temperatures some benzene was formed and in a few instances, a small amount of toluene appeared. In all runs, mixtures of unidentified aromatic products were also formed.

The origin of **8** is assumed to be dimerization of 1,3,6-bicyclo[3.2.0]heptatriene (**2**).[4,5] Formation of **2** finds further support in the identification of fulveneallene, albeit in low yield. The triene (**2**), in turn, strongly implicates 7-norbornadienylidene by analogy with the known rearrangement of **14** to **15**.[7l] Appearance of heptafulvalene at higher temperatures could be explained by either **2** crossing into the cycloheptatrienylidene manifold[22] or electrocyclic rearrangement of the dimer **8**. A sample of the latter was therefore isolated and pyrolyzed at 350 °C. At most, only a trace of heptafulvalene was formed. Benzene and toluene were not unexpected by analogy with their formation[24] from quadracyclanylidene **17** and probably signal formation of small amounts of atomic carbon. This point has yet to be fully explored.



14 15 16



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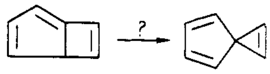
Finally, the complete absence of heptafulvalene at 400 °C is curious because it is known that this hydrocarbon survives these conditions when formed from phenylcarbene.[1] From this result it would appear that either **1** or **2** must be diverted at the higher temperature. Two possibilities are rearrangement of **2** to **17** or **10**, the former by analogy with the rearrangement of **16** to spiro[2,4]heptadiene[7l] and the latter due to the recent evidence for the high-temperature conversion of phenylcarbene to **10** via **2**.[6] Identification of **10** as a volatile product at this temperature is consistent with this suggestion but its yield was much lower than would be expected if this were a primary reaction.



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Thus, to summarize, it appears that pyrolysis of **7a** gives 7-norbornadienylidene. Between 200 and 400 °C this intermediate can lose carbon to give benzene or rearrange to bicyclo[3.2.0]heptatriene. This, in turn, can either dimerize or, if the temperature is high enough, cross into the cycloheptatrienylidene–cyclohepatetraene manifold. At 400 °C either **1** or **2** is thought to be side-tracked in an, as yet, undetermined manner.

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(12) All new compounds showed spectra consistent with the assigned structures. **7a** gave a satisfactory combustion analysis. **13a** was too unstable for combustion analysis.

(13) Cf. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967.

(14) B. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J. Chem. Soc., Perkin Trans. 1*, 2563 (1972).

(15) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919); R. A. Huisgen and H. Reimlinger, *Justus Liebigs Ann. Chem.*, **599**, 183 (1956).

(16) Attempts to sublime **7a** into the hot zone of a typical flash vacuum pyrolysis apparatus failed.

(17) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973).

(18) These structures were established by MS and comparison of their very characteristic NMR spectra with those reported for the known compounds.[4,5] Heptafulvalene was identified by comparison with authentic material.

(19) Formation of heptafulvalene from thermolysis of 7-norbornadienyl acetate at 450 °C has recently been mentioned[6] with the suggestion that 7-norbornadienylidene may be an intermediate. However, absence of heptafulvalene from thermolysis of **7a** above 400 °C as well as formation of diphenylcarbene products from thermolysis of 7-phenyl-7-norbornadienyl acetate[20] may signal a more complex mechanism.

(20) R. W. Hoffmann, R. Schuttler, and I. H. Loef, *Chem. Ber.*, **110**, 3410 (1977).

(21) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Am. Chem. Soc.*, **92**, 2147 (1970).

(22) The reverse of this reaction, closure of a cycloheptatetraene to a bicyclo[3.2.0]heptatriene, has also been suggested as one way to rationalize products from the dehalogenation of 11,11-dibromobicyclo[4.4.1]undecapentaene.[23]

(23) J. B. Carlton, R. H. Levin and J. Clardy, *J. Am. Chem. Soc.*, **98**, 6068 (1976).

(24) P. B. Shevlin and A. P. Wolf, *Tetrahedron Lett.*, 3987 (1970).

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Registry No. 1, 69705-23-3; 2, 23029-25-6; 7a, 70415-60-0; 8, 23057-33-2; 10, 27041-32-3.

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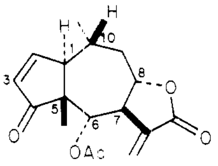
Helenanolides: Total Synthesis of *dl*-Bigelovin

Summary: A total synthesis of *dl*-bigelovin (1) is recorded which features as a key step a remarkable stereospecific reduction of hydroazulenone 3.

Sir: The helenanolides, which are characterized by the presence of a C(10) α-oriented methyl group and six chiral centers about a flexible hydroazulene ring system [e.g., bigelovin (1),[1] helenalin (2)[2]], belong to the pseudoguaianolide family of sesquiterpene lactones. Despite the fact that the relative and absolute configuration of numerous helenanolides have been known for many years, success at total synthesis has only been recorded on one previous occasion (cf. helenalin[3]). We wish to communicate herein the total synthesis of *dl*-bigelovin (1) which maintains complete stereochemical control during elaboration of the chirality at C(6), C(7), and C(8) on the hydroazulene ring system.



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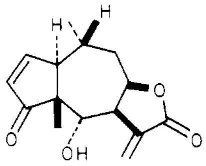

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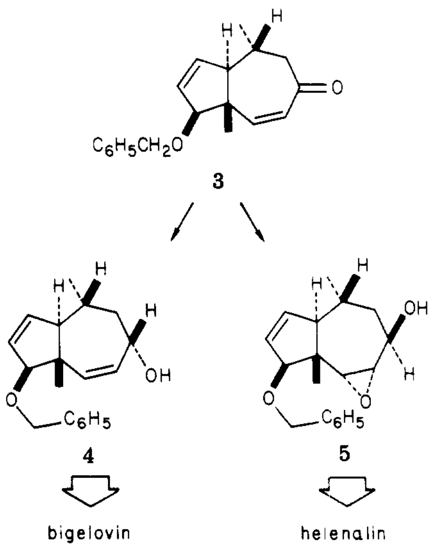
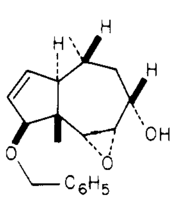
The key hydroazulenone intermediate 3, available through total synthesis,[3] upon reduction[4] with lithium aluminum hydride in tetrahydrofuran at 0 °C gave rise *exclusively in quantitative yield* to the crystalline allylic alcohol 4, mp 62–64 °C.[5] We were unable to find any evidence of hydride attack on the α-face of the carbonyl, which would have given rise to the corresponding C(8) isomeric allylic alcohol. This remarkable stereospecific reduction was unanticipated in view of our earlier efforts in the helenalin series. For example, we had previously established unambiguously that expoxidation (t-BuOOH, Triton B, THF) of enone 3 followed by reduction ($NaBH_4$, EtOH, 0 °C) afforded *exclusively* alcohol 5, mp 90–91 °C.[3]



With the configuration at C(8) assured, we proceeded with introduction of the remaining two chiral centers. Epoxidation of 4 employing m-chloroperbenzoic acid in methylene chloride provided in 65% yield the pure crystalline *syn*-epoxy alcohol 6, mp 99–100 °C. Elaboration of the γ-butyrolactone ring and cleavage of the benzyl ether were achieved by treatment of epoxide 6 with excess dilithioacetate[6] in dimethoxyethane (55 °C, 17 h) followed by direct addition of the intermediate trianion to a solution of lithium in liquid ammonia. Workup with 10% hydrochloric acid generated, as the sole product, tricyclic lactone 7: mp 186.0–188.5 °C; IR (KBr) 3475, 3350, 1765 cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 4.46 (ddd, 1 H, J = 3.2, 10.0, 11.8 Hz, H-8), 3.67 (d, 1 H, J = 8.7 Hz, H-6). The tetrahydropyranylated derivative of 7, prepared in 76% yield [dihydropyran, p-toluenesulfonic acid, methylene chloride, 0 °C, 1 h], was subjected to α-methylenation (61% overall yield) using the α-hydroxymethylation procedure:[7] (1) LDA, THF, HCHO, -20 °C; (2) MsCl, Py; (3) DBU, PhH. Cleavage of the tetrahydropyranyl ethers with 60% acetic acid (45 °C, 1.5 h) gave (82%) crystalline diol 8 (mp 152–153 °C; IR ($CHCl_3$) 3600, 3425, 1760 cm^{-1}), which upon oxidation with manganese dioxide in methylene chloride–benzene (2:1) (25 °C, 30 min) afforded a 77% yield of pure tricyclic enone 9: mp 186–187 °C; IR ($CHCl_3$) 3555, 1764, 1700 cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 7.77 (dd, 1 H, J = 6.4, 1.5 Hz), 6.24 (d, 1 H, J = 3.3 Hz), 6.14 (dd, 1 H, J = 6.4, 2.8 Hz), 6.02 (d, 1 H, J = 3.3 Hz)]. Acetylation (Ac_2O, Py, DMAP,[8] 25 °C, 3 h) of tricyclic alcohol 9 provided an 81% yield of pure crystalline *dl*-bigelovin (1), mp 195.5–197.5 °C, whose spectral properties



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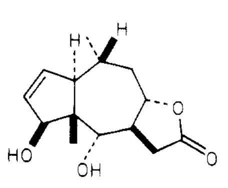

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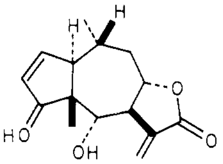

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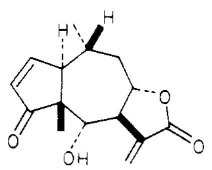

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(1) (a) Parker, B. A.; Geissman, T. A. *J. Org. Chem.* **1962**, *27*, 4127. (b) Herz, W.; Lakshmikantham, M. V. *Tetrahedron* **1965**, *21*, 1711.

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(3) Ohfune, Y.; Grieco, P. A.; Wang, C.-L. J.; Majetich, G. *J. Am. Chem. Soc.* **1978**, *100*, 5946.

(4) Identical results were obtained with sodium borohydride, diisobutylaluminum hydride, and lithium tri-*tert*-butoxyaluminum hydride.

(5) Professor Vandewalle (Ghent) has informed us of a similar observation using a related enone.

(6) Creger, P. L. *J. Org. Chem.* **1972**, *37*, 1907; cf. Danishefsky, S.; Schuda, P. F.; Kitahara, T.; Etheredge, S. J. *J. Am. Chem. Soc.*, **1977**, *99*, 6066; also see ref 3.

(7) Grieco, P. A.; Hiroi, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1317.

(8) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.