Double-Bond Isomers of Aromatic Compounds. 1-Methylene-1,2-dihydronaphthalene

Lawrence T. Scott* and William R. Brunsvold

Department of Chemistry, University of Nevada, Reno, Nevada 89557

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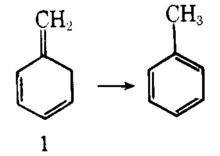
For many years, "isotoluene" (**1**) and its benzologues (**2** and **3**) were considered too unstable to isolate and characterize,[1-3] although such compounds have been proposed as intermediates in the Diels–Alder reaction of styrenes,[4] the autoinitiated polymerization of styrene,[5] and the all-carbon counterpart of the Claisen rearrangement.[6] Simple Hückel molecular orbital calculations[7] predict a substantial thermodynamic driving force for aromatization of **1**, **2**, and **3** (ΔE_π = 1.01β, 0.82β, and 0.75β, respectively). We describe herein a remarkable reaction which produces the previously unknown 1-methylene-1,2-dihydronaphthalene (**2**) and report some spectral and chemical properties of this new compound.



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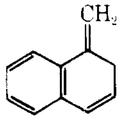
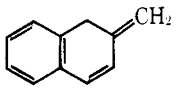
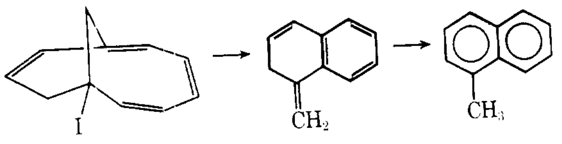




2 **3**

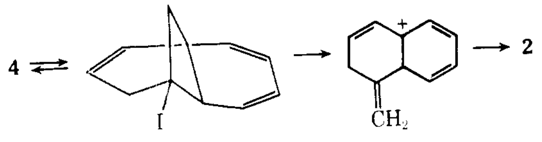
In the course of exploring synthetic routes to 1,5-methano[10]annulene,[8] we prepared 7-iodobicyclo[5.3.1]undeca-1,3,5,9-tetraene (**4**) and attempted to remove the elements of HI under various elimination conditions. To our surprise, treatment of iodotetraene **4** with the 18-crown-6 complex of potassium fluoride in hot benzene yielded hydrocarbon **2** contaminated with a small amount of α-methylnaphthalene, a product of further rearrangement.



4 **2**

1-Methylene-1,2-dihydronaphthalene (**2**) survives even chromatography on silica gel; however, it does aromatize rapidly and quantitatively to α-methylnaphthalene in the presence of trifluoroacetic acid. Spectral characteristics of **2** support the structural assignment: ^{1}H NMR (CCl_4) δ 7.5–6.7 (m, 4 H, ArH), 6.29 (d of t, J = 9, 2 Hz, 1 H, $CH{=}CHCH_2$), 5.83 (d of t, J = 9, 4 Hz, 1 H, $CH{=}CHCH_2$), 5.24 (m, 1 H, $C{=}CH_2$), 4.88 (m, 1 H, $C{=}CH_2$), 3.16 (m, 2 H, $CH_2CH{=}CH$); IR (neat) 888 (vs, $C{=}CH_2$), 1472 (m), 1625 (m), 3015 cm^{-1} (s); UV (hexane)[9] λ_{max} 238 and 281 nm; mass spectrum (20 eV) m/e 142 (M^+), fragmentation pattern identical to that of α-methylnaphthalene.

A plausible mechanism for the formation of hydrocarbon **2** from iodotetraene **4** involves initial electrocyclization followed by ionization of the cyclobutyl iodide **5** to give a stabilized homoallylic cation **6**; expulsion of a proton then completes the transformation. Related rearrangements of unbridged cyclooctatriene derivatives to styrene derivatives are well documented.[10]



5 **6**

Aromatization of hydrocarbon **2** by a simple [1,3] sigmatropic shift of hydrogen is disfavored electronically[11] in the suprafacial mode and sterically in the antarafacial mode. Early predictions,[1] of course, predated the development of the principle of orbital symmetry conservation.[11] Double bond isomers of aromatic compounds provide a dramatic illustration of the distinction between kinetic and thermodynamic stabilities.[12]

Experimental Section

1-Methylene-1,2-dihydronaphthalene (2). 7-Iodobicyclo[5.3.1.]undeca-1,3,5,9-tetraene[8] (**4**: 100 mg, 0.33 mmol), 95 mg of 18-crown-6 (0.36 mmol), and 110 mg of anhydrous potassium fluoride (1.9 mmol) were dissolved in 5 mL of dry benzene. The resultant orange solution was degassed and then heated to 80 °C with stirring under a nitrogen atmosphere for 5.5 h. The reaction mixture was diluted with 20 mL of petroleum ether, washed three times with 5 mL of saturated sodium chloride solution, and concentrated to an orange oil (72 mg). Preparative thin-layer chromatography on silica gel with petroleum ether gave 19 mg of a 9:2 mixture of **2** and α-methylnaphthalene (40% yield). See text for spectral data.

Registry No.—**2**, 68367-49-7; **4**, 68367-50-0; α-methylnaphthalene, 90-12-0.

References and Notes

(1) E. C. Horning, *Chem. Rev.*, **33**, 89 (1943); hydrocarbons **1**[2] and **3**[3] are now known.
(2) (a) W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962); (b) K. R. Kopecky and M.-P. Lau, *ibid.*, **43**, 526 (1978); (c) W. A. Pryor, W. D. Graham, and J. G. Green, **43**, 527 (1978).
(3) I. Murata, T. Nakazawa, M. Kato, T. Tatsuoka, and Y. Sugihara, *Tetrahedron Lett.*, 1647 (1975).
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(6) E. N. Marvell and C. Lin, *J. Am. Chem. Soc.*, **100**, 877 (1978), and references cited therein.
(7) We have taken ΔE_π as the difference in HMO energy between the isotoluene π-system and the corresponding aromatic π-system [A. Streitwieser, J. I. Brauman, and C. A. Coulson, "Supplemental Tables of Molecular Orbital Calculations", Pergamon Press, New York, 1965] ignoring alkyl substituent effects.
(8) L. T. Scott and W. R. Brunsvold, *J. Am. Chem. Soc.*, **100**, 4320, 6535 (1978).
(9) Compare with the stable 2,2-dimethyl derivative of **2**: λ_{max} 238 and 282 nm [G. Wittig, H. G. Reppe, and T. Eicher, *Justus Liebigs Ann. Chem.*, **643**, 47 (1961)].
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(12) We thank the University of Nevada Research Advisory Board and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Iron Pentacarbonyl Promoted Reductive Debromination of α-Bromo Ketones

Tien-Yau Luh,* Chi Hung Lai, Keng Lon Lei, and Shang Wai Tam*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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Reactions of iron carbonyls and α-halo ketones provide versatile routes for organic synthesis.[1-3] Several years ago, Alper and Keung[3a] found that α-halo ketones react with iron pentacarbonyl in refluxing 1,2-dimethoxyethane followed by

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