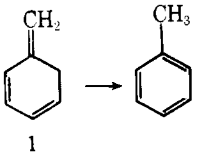
Double-Bond Isomers of Aromatic Compounds. 1-Methylene-1,2-dihydronaphthalene

Lawrence T. Scott* and William R. Brunsvold

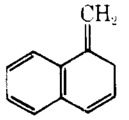
Department of Chemistry, University of Nevada, Reno, Nevada 89557

Received June 14, 1978

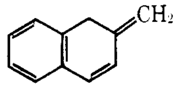
For many years, "isotoluene" (**1**) and its benzologues (**2** and **3**) were considered too unstable to isolate and characterize,[1-3] although such compounds have been proposed as intermediates in the Diels–Alder reaction of styrenes,[4] the autoinitiated polymerization of styrene,[5] and the all-carbon 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.



1

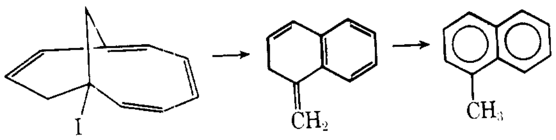


2



3

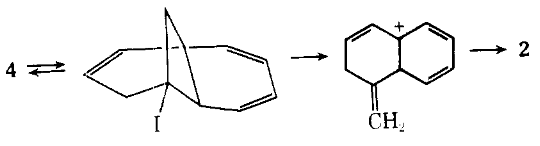
In the course of exploring synthetic routes to 1,5-methano[10]annulene,[8] we prepared 7-iodobicyclo[5.3.1]undeca-1,3,5,9-tetraene (**4**) and attempted to remove the elements of HI under various elimination conditions. To our surprise, treatment of iodotetraene **4** with the 18-crown-6 complex of potassium 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$_2$CH=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 cycloöctatriene 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).
(4) E. Ciganek, *J. Org. Chem.*, **34**, 1923 (1969), and referencee cited therein.
(5) W. A. Pryor and L. D. Lasswell, *Adv. Free-Radical Chem.*, **5**, 27 (1975); see, however, ref 2b and 2c.
(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)].
(10) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948); R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).
(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, Chapter 7.
(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*

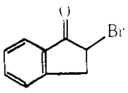
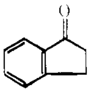
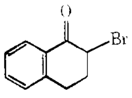
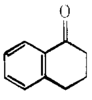
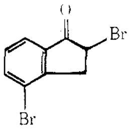
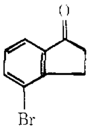
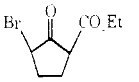
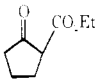
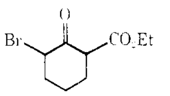
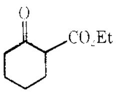
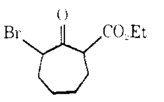
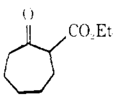
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Received August 22, 1978

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

0022-3263/79/1944-0641$01.00/0

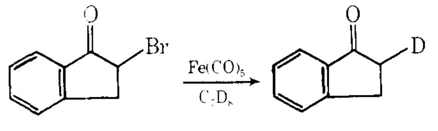
Table I. Reaction of α-Bromo Ketone and Iron Pentacarbonyl[a] in Xylenes

reactant	registry no.	product	registry no.	yield, %
PhC(=O)-CH_2Br	70-11-1	PhC(=O)-CH_3	98-86-2	57
	1775-27-5		83-33-0	55
	13672-07-6		529-34-0	56
	25834-53-1		15115-60-3	45
	42593-13-5		611-10-9	73
	30132-23-1		1655-07-8	68
	58729-55-8		774-09-0	54

[a] Registry no. 13463-40-6.

quenching with water to give a mixture of 1,4-diketones, monoketones, and/or β-epoxy ketones. They also reported that no reduced monoketone was isolated if the reaction mixture was worked up under strictly anhydrous conditions. In our laboratories, we carried out similar reactions in various solvents including 1,2-dimethoxyethane but obtained different results. With the use of slightly higher concentration of iron pentacarbonyl (twofold excess of iron pentacarbonyl), we found that α-bromo ketones can smoothly be reduced to the corresponding ketones without aqueous workup[4] in good yields; the results are summarized in Table I.

Organoiron halide complexes have been proposed as the intermediates for these reactions.[3a] In order to establish the mechanism for the reduction and to determine the origin of the hydrogen atom, we have studied the reaction in deuterated solvent. A mixture of 2-bromoindanone and iron pentacarbonyl in toluene-d_8 was refluxed and 2-deuterioindanone was obtained in 57% yield. In addition, if the reaction was carried out in xylene, or toluene, or 1,2-dimethoxyethane followed by using D_2O for reaction workup, no deuterium incorporation in the product (monoketone) was observed. The results of this study and related work[3b] suggest that the hydrogen source for these reactions could only arise from the solvent. It is well-known that the benzylic hydrogen is the good hydrogen donor for the radical abstraction reactions. These results tend to favor a free-radical mechanism.



In conclusion, this method provides a convenient procedure for reductive debromination of α-bromo ketones, in particular for preparation of a α-deuterio ketones. Furthermore, water may not be involved in these reactions.

Experimental Section[5]

General Procedure for the Reaction of Iron Pentacarbonyl with α-Bromo Ketones. A mixture of α-bromo ketone and a twofold excess of iron pentacarbonyl in xylene was refluxed for 4–6 h. The reaction mixture was cooled and filtered and the filter cake was washed with chloroform. The filtrate was evaporated in vacuo and the residue was chromatographed on neutral alumina using benzene or benzene–chloroform (1:1) as eluent.

Reaction with 2-Bromoacetophenone. A mixture of 2-bromoacetophenone (3.5 g, 17.6 mmol) and iron pentacarbonyl (6.9 g, 35.2 mmol) in xylene (100 mL) was refluxed for 4 h and the mixture was worked up according to general procedure to afford acetophenone (1.2 g, 57%) and 1,4-diphenylbutane-1,4-dione (0.02 g, 2%) identical in every respect with authentic samples.

Reaction with 2-Bromoindanone. 2-Bromoindanone (0.6 g, 2.8 mmol) and iron pentacarbonyl (1.1 g, 5.6 mmol) in xylene (75 mL) were refluxed for 4 h and then worked up according to general procedure to yield indanone (0.31 g, 55%), mp 40–41 °C (lit.[6] mp 40–41 °C).

Reaction with 2-Bromotetralone. A mixture of 2-bromotetralone (1.68 g, 7.5 mmol) and iron pentacarbonyl (2.9 g, 15 mmol) in xylene (50 mL) was transformed according to general procedure into tetralone (0.61 g, 56%), which gave identical spectroscopic properties with an authentic sample.

Reaction with 2,4-Dibromoindanone. A mixture of 2,4-dibromoindanone (0.3 g, 1 mmol) and iron pentacarbonyl treated in similar manner as described in the general procedure afforded 4-bromoindanone (96 mg, 45%), mp 93–94 °C (pentane) (lit.[7] mp 94–5 °C).

Reaction with Ethyl 5-Bromocyclopentanone-2-carboxylate. Ethyl 5-bromocyclopentanone-2-carboxylate (1.0 g, 4.3 mmol) was placed in xylene (30 mL), iron pentacarbonyl (1.5 g, 7.2 mmol) was added, and the reaction mixture was refluxed under nitrogen atmosphere for 6 h. The mixture was worked up as described previously to give ethyl cyclopentanone-2-carboxylate (0.49 g, 73%), which shows identical spectroscopic properties with authentic material.

Reaction with Ethyl 6-Bromocyclohexanone-2-carboxylate. A mixture of ethyl 6-bromocyclohexanone-2-carboxylate (3.25 g, 13 mmol) and iron pentacarbonyl (5.11 g, 26 mmol) in xylene (50 mL) was refluxed under nitrogen atmosphere for 6 h. The mixture was worked up according to general procedure to afford ethyl cyclohexanone-2-carboxylate (1.5 g 68%), identical in every respect with an authentic sample.

Reaction with Ethyl 7-Bromocycloheptanone-2-carboxylate. Ethyl 7-bromocycloheptanone-2-carboxylate (1 g, 3.8 mmol) was placed in xylene (30 mL), iron pentacarbonyl (1.5 g, 7.2 mmol) was added, and the reaction mixture was refluxed under nitrogen atmosphere for 6 h. The reaction mixture was worked up in the same manner as described previously to give ethyl cycloheptanone-2-carboxylate (0.38 g, 54%), identical in every respect with authentic compound.

Reaction of 2-Bromoindanone and Iron Pentacarbonyl in Toluene-d_8. 2-Bromoindanone (0.21 g, 1 mmol) and iron pentacarbonyl (0.4 g, 2 mmol) in toluene-d_8 (10 mL) were refluxed for 5 h. The mixture was worked up as usual to give monodeuterioindanone (0.075 g, 57%): NMR ($CDCl_3$) δ 2.65 (1 H, m), 3.15 (2 H, m), 7.2–7.8 (4 H, m); mass spectrum, m/e 133.

Registry No.—1,4-Diphenylbutane-1,4-dione, 495-71-6; monodeuterioindanone, 68475-32-1.

References and Notes

(1) R. Noyori, F. Shimizu, and Y. Hayakawa, *Tetrahedron Lett.* 2091 (1978), and earlier papers in this series.
(2) H. Alper in "Organic Syntheses via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, Eds., Wiley-Interscience, New York, 1977.
(3) (a) H. Alper and E. C. H. Keung, *J. Org. Chem.*, **37**, 2566 (1972); (b) S. J. Nelson, G. Detre, and M. Tanabe, *Tetrahedron Lett.*, 447 (1973).
(4) A recent report, however, showed that α-bromo ketone can be debrominated by diiron enneacarbonyl in aqueous DMF: R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi, and N. Sonada, *J. Am. Chem. Soc.*, **100**, 1759 (1978).
(5) All melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. NMR spectra were taken on a JEOL C-60 HL spectrometer. Mass spectra were measured on a Hitachi RMS-4 mass spectrometer.
(6) "Dictionary of Organic Compounds", Eyre & Spottiswoode, London, 1965.
(7) C. de Corral, *Rev. R. Acad. Cienc. Exactas, Fis. Nat. Madrid*, **51**, 103 (1957); *Chem. Abstr.*, **52**, 7257 (1958).