CHEMISTRY LETTERS, pp. 1103-1106, 1980.

SYNTHESIS OF 9,10-BENZOTETRACYCLO[5.3.0.0^{2,4}.0^{3,5}]DECA-1(7),9-DIEN-6-ONE, A VALENCE ISOMER OF BENZ[a]AZULEN-9(10H)-ONE

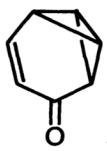
Yoshikazu SUGIHARA,* Takashi SUGIMURA, and Ichiro MURATA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

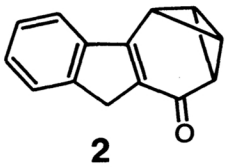
9,10-Benzotetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-1(7),9-dien-6-one (2), a valence isomer of benz[a]azulen-9(10H)-one (3), has been synthesized from 5,6-benzobicyclo[3.2.0]hepten-2-one utilizing the oxa-di-π-methane rearrangement.

In spite of the recent interest in the strained valence isomers of cyclic conjugated systems[1] the synthetic method of these compounds does not seem to be well established. This is mainly due to the fact that these isomers have a propensity for rearrangement to the corresponding cyclic conjugated systems which enjoy both relief of the strain energy and gain of the resulting conjugation energy. Furthermore, since the highly strained σ-bond is labile, functionalization of the molecule containing a bicyclobutane moiety must be devised.

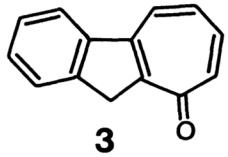
Recently, we reported the synthesis of tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (tropovalene) (1) from 3-acetoxybicyclo[3.2.0]hept-4-en-1-one using an oxa-di-π-methane rearrangement followed by elimination of acetic acid.[2] As a course of our study on valene type valence isomers of cyclic conjugated systems[2,3] we wish to present the synthesis of 9,10-benzotetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-1(7),9-dien-6-one (2), a valence isomer of benz[a]azulen-9(10H)-one (3).



1

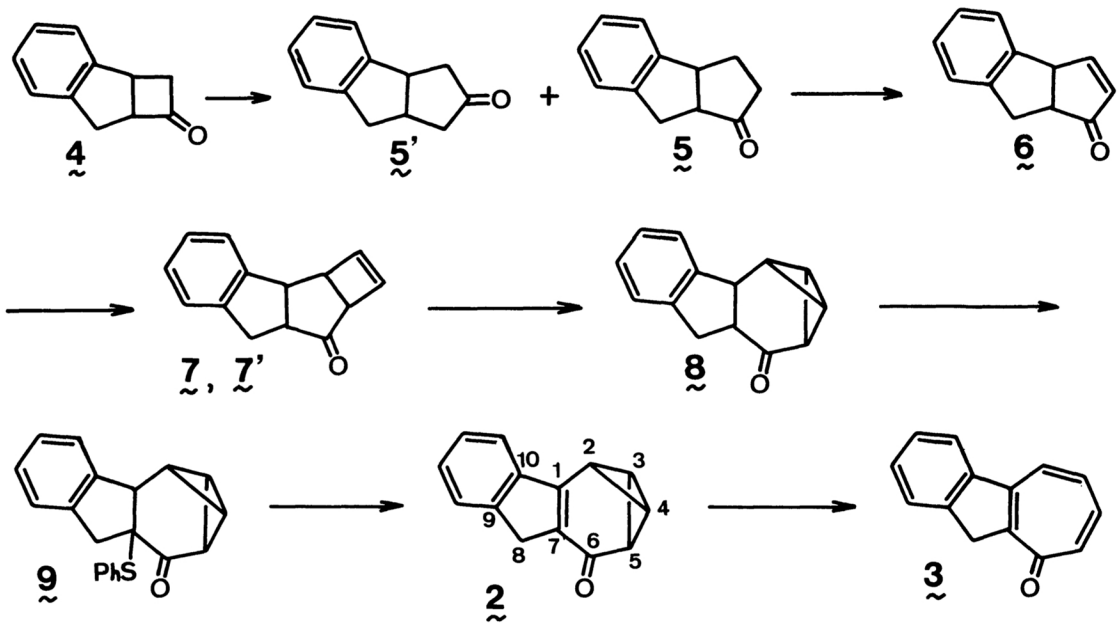


2



3

The compound 2 was prepared by the sequence of reactions shown in the following Scheme, part of which has been used in recent synthesis of 1. Ring expansion of the tricyclic ketone (4)[4] by treatment with ethyl diazoacetate in the presence of boron trifluoride (in ether, at r.t.) followed by heating in refluxing aqueous dioxane with potassium carbonate afforded a mixture of two isomeric five-membered ketones which were separated by column chromatography on silica gel to give 5 (60% yield, mp 32-33°C, $\nu_{C=O}$ 1721 cm^{-1})[5] and 5' (12% yield,



mp 33-34°C, $\nu_{C=O}$ 1720 cm^{-1}).[5]

Conversion of 5 into α,β-unsaturated ketone (6), mp 67-68°C, $\nu_{C=O}$ 1695 cm^{-1}, δ 7.83 (dd, 1H, J=5.3, 3.0 Hz), 6.74 (dd, 1H, J=5.3, 1.7 Hz), was carried out in 45% overall yield by the sequence[6] : (1) ketalization ($HOCH_2CH_2OH$, TsOH), (2) bromination (pyridinium hydrobromide perbromide, in tetrahydrofuran), (3) dehydrobromination (KOt-Bu in DMSO at r.t.), and (4) ketal cleavage with 4N HCl at 30°C.

The next stage of the synthesis involved the annelation of a cyclobutene ring to 6. Photochemical cycloaddition of 6 with dichloroethylene followed by ketalization ($HOCH_2CH_2OH$, TsOH), dechlorination (Na in liq. NH_3), and deketalization (2N HCl) produced a 10:1 mixture of the anti-isomer 7 (mp 86-87°C, $\nu_{C=O}$ 1722 cm^{-1}, δ 6.58 (d, 1H, J=2.5 Hz), 6.14 (dd, 1H, J=2.5, 1.0 Hz))[5] and syn-isomer 7' (liquid, $\nu_{C=O}$ 1724 cm^{-1}, δ 5.88 (m, 2H))[5] in 81.3% yield.[7] Either the anti- or syn-isomer, 7 or 7' was photolyzed in acetone using a 450 w high pressure mercury lamp for 3 and 6 h, respectively, to yield the bicyclobutane derivative 8, mp 56-57°C, $\nu_{C=O}$ 1694 cm^{-1}, δ 7.16 (m, 4H, aromatic), 3.72 (m, 1H, H-1), 3.40-2.70 (m, 5H, H-2,5,7,8), 2.48 (dt, 1H, J=10.0, 2.8 Hz, H-3 or 4), 2.26 (dtd, 1H, J=10.0, 2.8, 1.0 Hz, H-4 or 3), in 45% yield.

The final conversion of 8 into the desired tropovalene skeleton was accomplished by sulfenylation and dehydrosulfenylation reactions.[8] The ketone 8 was treated with LDA in THF and HMPA at -78°C, allowed to reach -10°C, then quenched into a solution of diphenyl disulfide in THF to give the phenylsulfide (9), $\nu_{C=O}$ 1698 cm^{-1}, δ 7.60-7.05 (m, 9H, aromatic), 3.84 (m, 1H, H-1), 3.52(d, 1H, J=16.5 Hz, H-8), 3.30 (d, 1H, J=16.5 Hz, H-8), 3.04-2.75 (m, 2H, H-2 and 5),

Table I ^{1}H- and ^{13}C-NMR data of 2 [a]

^{1}H-NMR			^{13}C-NMR[b] in $CDCl_3$	
in $CDCl_3$	in $CDCl_3$+C_6D_6 (1:1)	Assignment	sp^3-C	sp^2-C
7.70-7.15(m, 4H)	7.11(m, 4H)	Ar-H	30.8(213) C-3,4	121.2, 124.9
3.50(m, 2H)	3.34(s, 2H)	H-8	32.6(161) C-2	126.8, 128.6
3.50(m, 2H)	3.02(t, 2H)	H-3,4,J=2.3	33.9(132) C-8	129.7, 141.8
3.22(dt, 1H)	2.78(dt, 1H)	H-5,J=4.0,2.3	48.2(161) C-5	145.0, 160.0
2.82(dt, 1H)	2.68(dt, 1H)	H-2,J=4.0,2.3		193.9 C-8

a) chemical shifts are recorded in δ downfield from internal TMS.
b) coupling constants with directly bonded hydrogens are given in parentheses in Hz.

2.60 (dt, 1H, J=9.2, 2.7 Hz, H-3 or 4), 2.42 (dtd, 1H, J=9.2, 2.7, 1.1 Hz, H-4 or 3), which, on oxidation with m-chloroperbenzoic acid (CH_2Cl_2, -78°C) and pyrolytic dehydrosulfenylation (in CCl_4 at 50°C, 20 min), gave the desired compound 2 in 40% yield after chromatography on deactivated silica gel with benzene. The evidence that the product was indeed 2 rests chiefly upon its spectral data: 2 showed fairly low carbonyl band at 1638 cm^{-1} in its IR spectrum,[2] and the MS spectrum exhibited peaks at *m/e* 194 (M^+, 42%), 156 (fluorene cation, 68%) and 155 (fluorenyl cation, 100%). The ^{1}H-NMR spectrum of 2 in $CDCl_3$ exhibited a pair of doublet of triplets at δ 2.82 and 3.22 along with aliphatic protons multiplet at δ 3.50 (4H) and aromatic protons multiplet at δ 7.15-7.70 (4H). Although we cannot, from these data, confirm the bicyclobutane structure of 2, it could be easily seen from its ^{1}H-NMR spectrum in a 1:1 mixture of $CDCl_3$ and C_6D_6. Thus, all of the signals attributable to the aliphatic protons were clearly separated and appeared at δ 2.68 (dt, 1H, J=4.0, 2.3 Hz, H-2), 2.78 (dt, 1H, J=4.0, 2.3 Hz, H-5), 3.02 (t, 2H, J=2.3 Hz, H-3 and 4), 3.34 (s, 2H, H-8,8). The considerably large coupling constant (d, J=4.0 Hz) observed in the pair of doublet of triplets is characteristic of a long-range interaction between two wing protons of a bicyclobutane skeleton.[2,3c,g,i] The ^{13}C-NMR data shown in Table I is also consistent with the proposed tropovalene structure.[3j]

Irradiation of a solution of 2 in acetone with a 450 w high pressure mercury lamp produced benz[a]azulen-9(10H)-one (3), structure of which was based on its MS (m/e 194.0689), IR ($\nu_{C=O,C=C}$ 1625, 1570, 1555 cm^{-1}), ^{1}H-NMR (δ 4.07 (2H, s), 7.0-7.8 (8H, m)), and UV spectra (CH_2Cl_2: 276, 284 (sh), 320 nm).

Reactions of 2 and synthesis of 8,9-benzo derivative and parent compound are in progress.

This investigation was supported in part by a Grant-in-Aid for Scientific Research (NO. 343007) from the Ministry of Education, Science, and Culture.

References and Notes

1) See for example, A. Greenberg and J. F. Liebman, "Strained Organic Molecules," Academic Press, Inc., New York, N.Y., 1978.
2) Y. Sugihara, N. Morokoshi, and I. Murata, *Tetrahedron Lett.*, 1977, 3887.
3) (a) I. Murata and K. Nakasuji, *Tetrahedron Lett.*, 1973, 47. (b) I. Murata, K. Nakasuji, and H. Kume, *ibid.*, 1973, 3401, 3405. (c) I. Murata, T. Tatsuoka, and Y. Sugihara, *ibid.*, 1973, 4261. (d) I. Murata, T. Tatsuoka, and Y. Sugihara, *Angew. Chem. Intern. Ed.*, 13, 142 (1974). (e) C. Kabuto, T. Tatsuoka, I. Murata, and Y. Kitahara, *ibid.*, 13, 669 (1974). (f) I. Murata, T. Tatsuoka, and Y. Sugihara, *Tetrahedron Lett.*, 1974, 199. (g) I. Murata, T. Nakazawa, M. Kata, T. Tatsuoka, and Y. Sugihara, *ibid.*, 1975, 1647. (h) T. Tatsuoka and I. Murata, *Bull. Chem. Soc. Jpn.*, 49, 825 (1975). (i) M. Uyegaki, S. Ito, Y. Sugihara, and I. Murata, *Tetrahedron Lett.*, 1976, 4473. (j) Y. Sugihara, N. Morokoshi, and I. Murata, *Chem. Lett.*, 1979, 745.
4) L. R. Krepski and A. Hassner, *J. Org. Chem.*, 42, 2879 (1978).
5) All new compounds described in this paper gave satisfactory elemental analyses.
6) P. E. Eaton, R. H. Mueller, G. R. Carlson, D. A. Cullison, G. F. Cooper, J-C. Chou, and E. P. Krebs, *J. Am. Chem. Soc.*, 99, 2751 (1977).
7) The stereochemistry of the syn- and anti-isomers have not been elucidated.
8) B. M. Trost, T. N. Salzman, and K. Hiroi, *J. Am. Chem. Soc.*, 98, 4887 (1976).

(Received June 27, 1980)