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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

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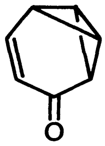
9,10-Benzotetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-1(7),9-dien-6-one (**2**), a valence isomer of benz[a]azulen-9(10H)-one (3), has been synthesized from 5,6-benzobicyclo[3.2.0]hepten-2-one utilizing the oxa-di-π-methane rearrangement.

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**).



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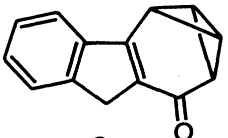

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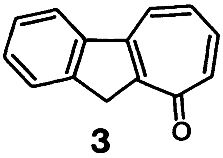

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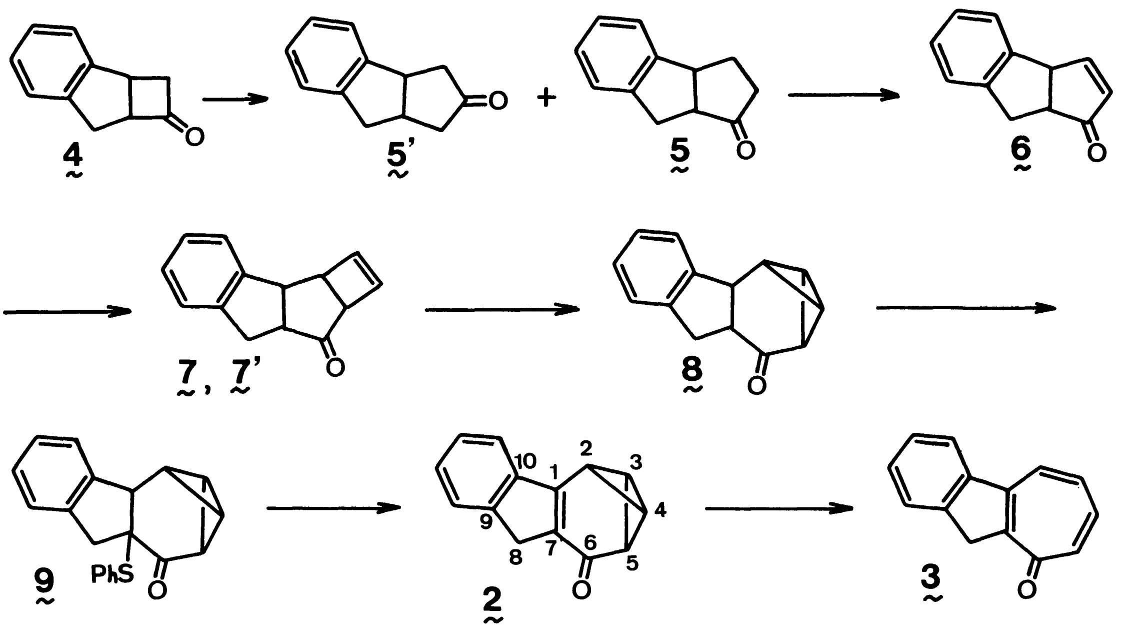
The compound **2** was prepared by the sequence of reactions shown in the following Scheme, part of which has been used in recent synthesis of **1**. Ring expansion of the tricyclic ketone (**4**)[4)] by treatment with ethyl diazoacetate in the presence of boron trifluoride (in ether, at r.t.) followed 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.

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