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THE TRICYCLO$[5.2.0.0^{2,9}]$NONA-3,5-DIENE SYSTEM (HOMOOCTAVALENE)[1]

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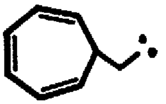
In our previous reports[2] on Bamford-Stevens reaction of tropyl acetoaldehyde tosylhydrazones, β-(2,4,6-cycloheptatrien-1-yl)ethylcarbenes <u>1</u> have been reported to give the C_9H_{10} hydrocarbons, bicyclo[4.2.1]nona-2,4,7-trienes <u>2</u> and tricyclo-$[3.3.1.0^{2,8}]$nona-3,6-dienes <u>3</u>. For the mechanistic pathway of the formation of <u>2</u>, tetracyclo$[4.3.0.0^{2,9}.0^{5,7}]$non-3-enes <u>4</u>[3] and tricyclo$[5.2.0.0^{2,9}]$nona-3,5-dienes <u>5</u> as well as <u>3</u> have been proposed as possible intermediates.[2a] Among them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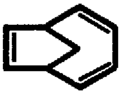
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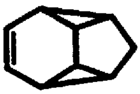
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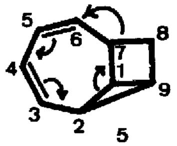
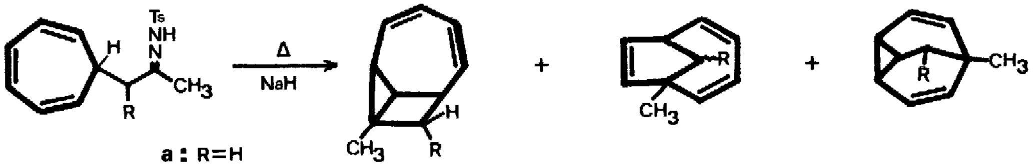


<u>5</u>

<u>3</u> was discarded by the control experiment[2a] and a thermally labile product <u>4</u> was best explained.[2c] However, <u>4</u> and <u>5</u> have never been isolated and an alternative pathway via <u>5</u> could not be completely excluded. Because of the high strain of <u>5</u>, <u>2</u> can be presumably obtained from <u>5</u> either by a concerted [1,7]-sigmatropic shift[4] or by a diradical pathway. It, therefore, seems intriguing to isolate and subject <u>5</u> to the pyrolysis in order to clarify the real intermediate for the formation of <u>2</u> from <u>1</u>. Herein we wish to report the first isolation, independent synthesis and pyrolysis of the title compounds.

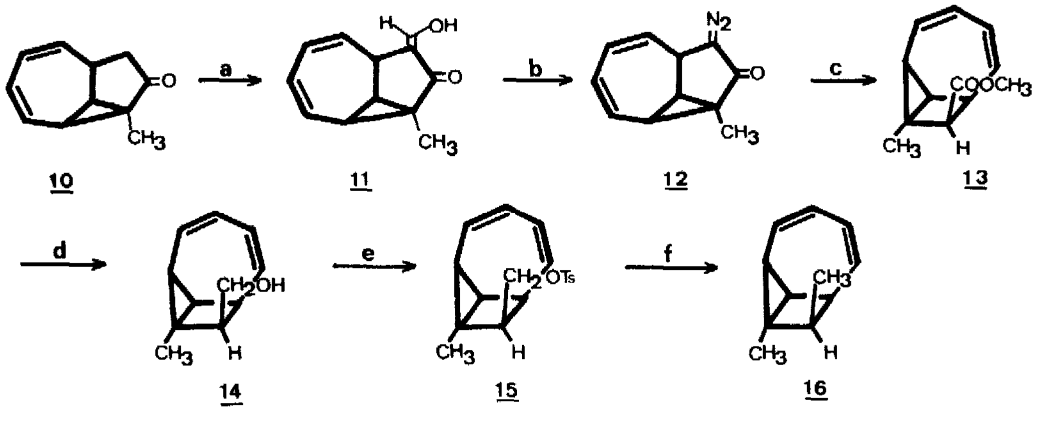
The decomposition of the sodium salt of <u>6a</u> (mp 162°, dec)[5] in diglyme at 150° gave a mixture of $C_{10}H_{12}$ hydrocarbons which upon separation by vpc (Carbowax 20M, Chromosorb W) afforded <u>7a</u> (7 %), <u>8a</u> (41 %) and <u>9a</u> (34 %). Similarly, the pyrolysis of <u>6b</u> (mp 150°, dec) gave a mixture of <u>7b</u> (9 %), two isomers of <u>8b</u> (9-endo-methyl, 15.4 %; 9-exo-methyl, 7.6 %) and <u>9b</u> (28 %). The structures of <u>8</u> and <u>9</u> were unambiguously determined by pmr spin decoupling and comparisons of their pmr



a: R=H
b: R=CH_3

<u>6</u> <u>7</u> <u>8</u> <u>9</u>

with those of the reported methyl or phenyl derivatives[2c] of 2 and 3. On the other hand, the structural elucidation of the previously unknown tricyclo-[5.2.0.0^{2,9}]nona-3,5-diene system for 7 was derived from the following uv and pmr spectral evidences. 7a : uv (cyclohexane), 276 nm (max, log ε=3.58); nmr (CCl$_4$), 1.59 (dd, 4.7 and 4.7 Hz, C$_1$-H), 1.30 (C$_2$-H), 5.6-6.2 (multiplet, C$_3$, C$_4$, C$_5$, C$_6$-H), 2.8-3.1 (multiplet, C$_7$-H), 2.02 (broad d, C$_8$-H), 1.30 (s, C$_9$-methyl). 7b : uv (cyclohexane), 277 nm (max, log ε=3.70); nmr (CCl$_4$), 1.59 (dd, 4.5 and 5.0 Hz, C$_1$-H), 1.36 (dd, 5.0 and 5.5 Hz, C$_2$-H), 6.08 (dd, 5.5 and 12.3 Hz, C$_3$-H), 5.68-5.75 (multiplet, C$_4$, C$_5$, C$_6$-H), 2.15-2.40 (multiplet, C$_7$, C$_8$-H), 1.16 (d, 6.7 Hz, C$_8$-methyl), 1.22 (s, C$_9$-methyl) ppm. The uv absorption maxima in 7a and 7b shifted bathochromically about 17 nm as compared with that of tricyclo-[5.3.0.0^{2,10}]deca-3,5-diene.[6] These distinctive uv shifts should be attributed to the ring strain and more favorable conjugation effect of cyclopropane ring which results from the incorporation of cyclobutane. Although the coupling constants, $J_{1,2}$=4.7 Hz in 7a and 5.0 Hz in 7b seem rather small as the cis coupling in cyclopropane, these are reasonable values in bicyclopentane system since the value of 5.52 Hz is observed in bicyclopentane derivative.[7] Since the coupling constant, $J_{7,8}$ in 7b was not read clearly, the configuration of C$_8$-methyl could not be decided from pmr spectrum. However, spectral evidences to support these structures and the exo configuration of C$_8$-methyl in 7b were obtained by the comparisons of spectral data with those of 8-endo-methyl-tricyclo[5.2.0.0^{2,9}]nona-3,5-diene 16 which was synthesized by the scheme outlined below.



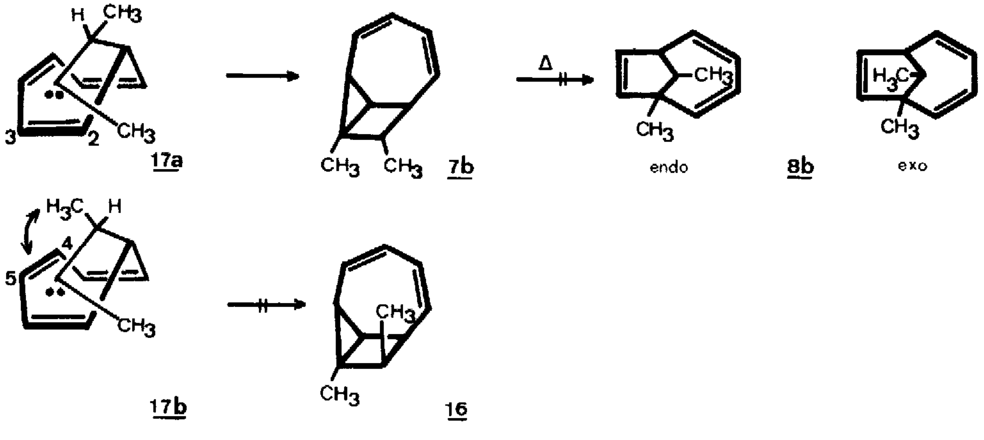
a : HCO$_2$C$_2$H$_5$, NaH; b : TsN$_3$; c : 450 W; d and f : LiAlH$_4$; e : TsCl

Ketone 10[8] was prepared by the procedure of Doering[6] and diazoketone 12 (mp 58°)[9] was obtained from 11[10] by diazo transfer reaction.[11] Upon irradiation of 12 in methanol at 60°, 13 was isolated in 54 % yield. 13 : ir (neat), 1735 cm^{-1}; uv (ethanol), 233 (sh, log ε=3.33), 275 (max, log ε=3.47), 314 (sh, log ε=2.50) nm; nmr (CCl$_4$), 1.68 (dd, 5.0 and 5.0 Hz, C$_1$-H), 1.35 (dd, 5.0 and 6.0 Hz, C$_2$-H), 5.95 (dd, 6.0 and 12.0 Hz, C$_3$-H), 5.75 (dd, 6.0 and 12.0 Hz, C$_4$-H), 5.64 (dd, 6.0 and 13.0 Hz, C$_5$-H), 5.55 (dd, 6.0 and 13.0 Hz, C$_6$-H), 3.20 (ddd, 5.0, 6.0 and

10.0 Hz, C_7-H), 3.04 (d, 10.0 Hz, C_8-H), 3.40 (s, C_8-COOC$\underline{H}_3$), 1.40 (s, C_9-methyl) ppm. Tosylate 15 (mp 56-7°)[12] was obtained from alcohol 14[13] in 96 % yield and the reduction of 15 followed by separation (Carbowax 20M, Chromosorb P) gave 16 as a colorless oil. The mass spectrum of 16 was completely the same as that of 7b, and 16 has the following spectral properties : uv (cyclohexane), 281 nm (max, log ε =3.55); m/e, 146 (M^+), 131, 91; nmr (CCl_4), 1.60 (dd, 5.0 and 5.0 Hz, C_1-H), 1.21 (dd, 5.0 and 6.0 Hz, C_2-H), 6.15 (dd, 6.0 and 12.0 Hz, C_3-H), 5.84 (dd, 6.0 and 12.0 Hz, C_4-H), 5.52 (dd, 6.0 and 10.0 Hz, C_5-H), 5.56 (dd, 10.0 Hz, C_6-H), 3.28 (ddd, 5.0, 10.0 and 10.0 Hz, C_7-H), 2.66 (dq, 7.0 and 10.0 Hz, C_8-H), 0.87 (d, 7.0 Hz, C_8-methyl), 1.26 (s, C_9-methyl)ppm. An unequivocal determination of the endo configuration at the C_8 position was based on the large coupling constant, $J_{7,8}$ (10.0 Hz in 13 and 16). The high field absorption of the methoxy at 3.40 ppm in 13 and the methyl group at 0.87 ppm in 16 also provide the endo configuration at the C_8 position. On the contrary, the low field absorption of the C_8-methyl at 1.16 ppm in 7b clearly indicates the exo configuration at the C_8 position in 7b. Thus, the comparison of the spectral data of 7a and 7b with those of 16 establishes the homooctavalene skelton for 7.

In the decomposition of 6b, the stereospecific formation of 7b and nonstereospecific one of 8b are noteworthy. A thermally allowed suprafacial [1,7]-sigmatropic rearrangement of 7b with inversion of configuration should give 8-endo-methyl 8b and therefore, if 7b were an intermediate, a diradical pathway from 7b would be presumed for the nonstereospecific formation of 8b. However, the pyrolysis of 7b in diglyme at 150° and 220° did not give either 8-endo-methyl 8b or 8-exo-methyl 8b, and 7b was completely recovered. Same results were obtained in 7a. These results completely ruled out the intermediacy of 5 for the formation of 2 from 1.

The stereospecific formation of 7b from 6b can be well explained in terms of the degree of the steric hindrance in a transition state 17. Because of the steric hindrance between the α-methyl group and the C_4-C_5 double bond in 17b, 17b which might give 16 is unfavorable while in the less hindered 17a the carbene



adds to the C_2-C_3 double bond to give 7b without big sterical restriction.

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(8) 10 : bp 96°/0.6 mmHg; ir (neat), 1720 cm^{-1}; uv (ethanol), 260 nm (max, log ε=3.14); nmr (CCl_4), 3.11 (m), 2.32 (dd, 9.0 and 19.0 Hz), 2.10 (dd, 6.0 and 6.0 Hz), 1.88 (dd, 6.0 and 6.0 Hz), 1.80 (dd, 10.0 and 19.0 Hz), 1.29 (s) ppm.

(9) 12 : ir (KBr), 2070, 1670 cm^{-1}; uv (ethanol), 250 (max, log ε=4.08), 298 (sh, 3.66), 400 (max, 1.5) nm; nmr (CCl_4), 2.2 (dd, 7.0 and 7.0 Hz, 1H), 1.8 (dd, 3 and 7 Hz, 1H), 5.7-6.5 (m, 4H), 4.3 (m, 1H), 1.32 (s, 3H).

(10) 11 : mp 113°; ir (KBr), 3020, 2900, 1680 cm^{-1}; uv (ethanol), 261 (max, log ε=4.08), 310 (max, 3.55) nm; nmr ($CDCl_3$), 2.30 (dd, 7 and 7 Hz, 1H), 1.80-2.02 (m, 1H), 5.75-6.50 (m, 4H), 3.76 (dd, 7 and 7 Hz, 1H), 1.38 (s, 3H), 6.96 (s, 1H), 10.1 (s, 1H) ppm.

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(12) 15 : ir (KBr), 1350-1170 cm^{-1}; uv (ethanol), 224.5 (max, log ε=4.08), 274 (max, 3.49) nm; nmr ($CDCl_3$), 1.59 (dd, 4.5 and 4.5 Hz, 1H), 1.18 (dd, 4.5 and 6.5 Hz, 1H), 5.77-6.22 (m, 4H), 2.93-3.35 (m, 1H), 2.68-2.88 (m, 1H), 3.92 (dd, 3.0 and 5.0 Hz, 2H), 1.20 (s, 3H), 7.76 (d, 8 Hz, 2H), 7.35 (d, 8 Hz, 2H), 2.38 (s, 3H) ppm.

(13) 14 : bp 120°/0.1 mmHg (bath temp); ir (neat), 3400 cm^{-1}; uv (ethanol), 216 (max, log ε=3.67), 277 (max, 3.47) nm; nmr ($CDCl_3$), 5.46-5.90 (m, 4H), 3.50 (d, 2.0 Hz, 1H), 3.47 (s, 1H), 3.0-3.4 (m, 1H), 2.45-2.95 (m, 1H), 1.63 (dd, 4.5 and 4.5 Hz, 1H), 1.25 (dd, 4.5 and 6.0 Hz, 1H), 1.32 (s, 3H) ppm.