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[7]- AND [9](3,5)TROPONOPHANES AND THE CORRESPONDING HYDROXYTROPYLIOPHANES

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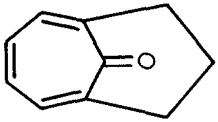
Abstract: Synthesis, physical and chemical properties of the title compounds are described. Attempted synthesis of the next lower homologs were unsuccessful.

In the previous papers[1)], the result of our systematic studies on a series of 2,7-bridged troponophanes was reported. In the lower homologs with a 3 or 4-carbon bridges (e.g. **1**[1c)], **2**[1b)]), the tropone ring is bent to a tub form with narrow interior bond angles, pyramidalization of sp^2 carbons, and reduced conjugation between the carbonyl group and the triene system. The success in the synthesis of such deformed tropones depends on the fact that tropone has little extra delocalization of its π-electrons other than a normal conjugated ketone system[2)] and the bonds connecting the carbonyl group therefore have very small double bond character. As the extension of the study on distorted tropones, we have attempted to synthesize another series of metatroponophanes which inevitably contain a "bridge-head" double bond. We describe herein the synthesis, some physical properties and chemical behavior of [7]- and [9](3,5)troponophanes (**3a** and **3b**) and attempted synthesis of [6] homolog (**3c**).



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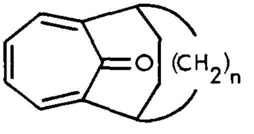
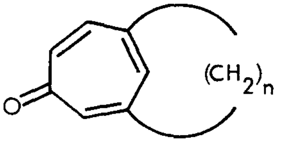


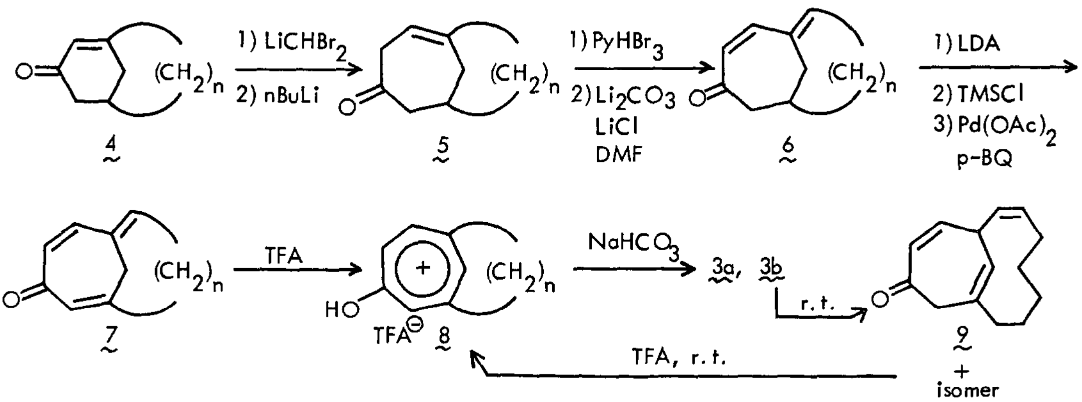
2 (n=1, 2)



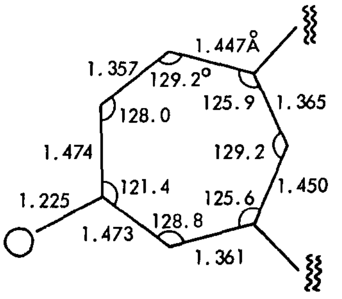
3a: (n=9)
b: (n=7)
c: (n=6)

Synthesis The synthesis of all the series (**a**, **b**, **c**) followed the reaction sequence shown on next page. To the cycloheptanones **5** prepared (**a**: 50%, **b**: 38%, **c**: 37%) by the ring enlargement[3)] of the cyclohexanones **4**[4)], two double bonds were introduced in two stages [bromination-dehydrobromination to the dienones **6** (**a**: 39%, **b**: 59%, **c**: 31%) and the Pd-catalyzed oxidation of their silyl enol ethers[5)]] to give the trienes **7** (**a**: 39%, **b**: 59%, **c**: 15%). Acid treatment (CF_3CO_2H, 60°C, 3hr-10hr) of **7a** and **7b** yielded the corresponding tropylium ions **8** which on neutralization afforded the desired **3** (**a**: colorless prisms, m.p. 84-85.5°C, **b**: colorless liquid, both 58% yield from **7**). However, **7c** did not produce **8c** under the same conditions and was recovered unchanged on neutralization[6)]. While **3a** is stable, 3b rearranges on standing at room temperature to the double bond isomers, **9** and another ketone, reflecting the significant destabilization of the tropone ring. The isomers regenerate **8b** slowly by the acid treatment[7)]. These observations disclosed the relative stability of **3**, **7** and **8** in each series.

Deformation of Tropone Ring in **3** Since **3b** is a liquid, the molecular mechanics calculations

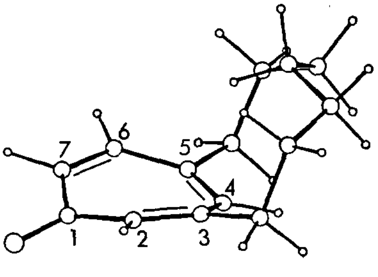


(MMPI)[9] were performed on both 3a and 3b. While the tropone ring in 3a assumes a near planar conformation, that in 3b is clearly distorted in an irregular tub form with increased bond alternation and contracted interior bond angles, compared with planar tropone[10] (Fig. 1). The largest torsional angle around the double bond is 12.7° at $C_4=C_5$.



a: Bond angles and bond lengths

dihedral angle	θ
C_1-C_2, C_3-C_4	2.2°
C_2-C_3, C_4-C_5	30.3°
C_3-C_4, C_5-C_6	12.7°
C_4-C_5, C_6-C_7	16.7°
C_5-C_6, C_7-C_8	6.6°
C_6-C_7, C_1-C_2	27.0°
C_7-C_1, C_2-C_3	32.1°



b: Perspective view

Fig. 1 Structural parameters and shape of 3b calculated by MMPI

Deformation of the tropone ring in 3b has small but significant effect on its NMR spectra shown in Table 1 together with those of 3a. On going from 3a to 3b, the carbonyl carbon (C-1) shift down field, while all olefinic carbons and hydrogens shift slightly upfield in general. This may reflect the decreased conjugation between the carbonyl group and the triene system as in 1 and its homologs[1]. The largest shifts appear at C_4 (1.6 ppm upfield) and H_4 (0.24 ppm downfield) which may be associated with the largest strain imposed by the bridges. The reduced conjugation in 3b indicated above in NMR, is too small to be revealed in electronic spectra[8], when compared with that of 3,5-dimethyltropone 11[11]. Contracted interior carbonyl angle is shown by IR spectra [ν 1583 (11), 1582 (3b) and 1596 cm^{-1}

Table 1. NMR chemical shifts of 3a and 3b

positions		1	2	3	4	5	6	7
3a	C	186.7	138.2*	151.9	138.0*	146.6	139.1*	141.5
	H	—	6.88	—	6.94	—	6.95	6.98
3b	C	187.4	137.1	151.9	136.4	145.9	138.9	140.6
	H	—	6.77	—	7.18	—	6.94	6.93

*tentative assignment

(3b), all in CCl_4].

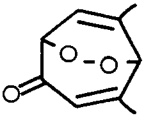
Conformation of bridges PMR spectra of 3a and 3b exhibit triplets due to the "benzylic" protons, disclosing free flipping of the bridge in both cases. Furthermore, a 2H quintet is visible for 3b at a very high field (0.92 ppm) as in [7]metacyclophane 12[12], supporting the stable conformation shown in Fig. 1b. From its coalescence temperature, -93°C, $\Delta G^{\ddagger}$ for the flipping was estimated to be 8.3 kcal/mol, the value smaller than that of 12 ($\Delta G^{\ddagger}$ 11.5 kcal/mol) and the 5-membered ring heterophanes ($\Delta G^{\ddagger} \geq 18.2$ kcal/mol)[13], again disclosing the effect of aromatic ring size[13].

Tropyliophanes 8 Tropyliophanes 8a and 8b were prepared from 3a and 3b by the acid treatment (CF_3CO_2H, r.t.). Their NMR spectra (Table 2) disclosed the almost complete delocalization of positive charge in 7-membered rings as is indicated by the following observation: All hydrogens, C_3 and C_6 appear at lower field than in neutral species (Table 1), while C_1, C_2 and C_7 show upfield change. This is exactly what happens in 11 on protonation[11]. The formation of tropylium ion species is also demonstrated by electronic spectra[8]. Although some bathochromic shift is observed in 8a and 8b compared with the protonated 11, all three exhibit two strong bands characteristic of tropylium ion.

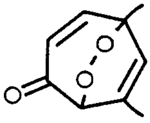
Table 2. NMR chemical shifts of the tropyliophanes

positions		1	2	3	4	5	6	7
8a	C	179.8	137.7	172.6	150.1	165.5	152.0	139.3
	H	—	8.13	—	8.48	—	8.35	8.19
8b	C	180.2	136.8	171.6	150.7	163.6	152.3	139.4
	H	—	8.09	—	8.88	—	8.36	8.19

Photooxygenation of 3 Since deformation of the tropone ring is indicated in 3, photooxygenation reaction, known to give an endoperoxide from tropone[14], was carried out (O_2, hν, hematoporphyrin, acetone) with the hope that the unsymmetrical bridging may differentiate two reacting diene sites and change the product distribution (A : B). The result is shown in Table 3.



A



B

Table 3. Photooxygenation of 3 and 11

compds	products	yields	ratios (A : B)
11	13A + 13B	94%	3 : 7
3a	14Aa + 14Ba	79%	8 : 2
3b	14Ab	89%	10 : 0

The reaction is clearly controlled by the conformation of the tropone ring, reflecting in the energy difference in transition states.

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6) NMR spectrum of 7c in D_2SO_4 at room temperature exhibits a signal at 8.9 ppm but the recovered 7c contained deuterium atoms at C_2, C_4 (d_2) and C_7 in addition to d_2 in the bridge methylene.

7) Molecular mechanics calculations (MMPI)[9] disclosed the strain energy situation in these compounds: 7b (SE=45.8 kcal/mol) is less stable than 3b (42.1 kcal/mol), which in turn is less stable than 9 (37.6 kcal/mol). However 7c (SE=30.2 kcal/mol) is more stable than 3c (46.2 kcal/mol).

8) All the new compounds described in this paper are all colorless liquids unless otherwise stated and gave satisfactory elemental analyses. The spectra were measured under the following conditions unless otherwise stated: UV in cyclohexane, IR in KBr or liq film, NMR in $CDCl_3$. The selected physical properties follow: 3a: λmax 216 (log ϵ 4.16), 232 (4.28), 290 (3.48 sh), 303 (3.79), 317 nm (3.73 sh), 3b: λmax 219 (log ϵ 4.10 sh), 234 (4.18), 304 (3.71), 318 nm (3.62 sh), 7a: m/e 230 (M^+, bp) ν 1638, 1603 cm^{-1}, δ 0.8-1.9 (12H, m), 2.2-2.5 (4H, m), 3.20 (2H, s), 5.65 (1H, t, J=9.0), 5.98 (1H, d, J=11.5), 6.03 (1H, s), 6.77 (1H, d, J=11.5), 7b: m/e 202 (M^+), 104 (bp), ν 1632, 1600 cm^{-1}, δ 1.0-2.6 (12H, m), 3.29 (2H, s), 5.78 (1H, dd, J=10.1, 8.3), 5.97 (1H, dd, J=11.5, 1.4), 6.02 (1H, s), 6.84 (1H, d, J=11.5), 7c: colorless prisms, m.p. 45-48°C, m/e 188 (M^+, bp), ν 1638, 1601 cm^{-1}, δ 1.1-3.0 (10H, m), 2.98 (1H, d, 12.2), 3.16 (1H, d, 12.2), 5.73 (1H, t, J=7.9), 5.95 (1H, s), 5.98 (1H, d, J=11.9), 6.92 (1H, d, J=11.9), 8a: λmax (50% H_2SO_4) 246 (log ϵ 4.34), 321 nm (3.84), 8b: λmax (50% H_2SO_4) 247 (log ϵ 4.45), 324 nm (3.94), 9: δ 1.10-2.60 (m), 3.09 (2H, br.s), 3.36 (1H, dd, 7.0, 1.8), 5.72 (1H, br.d, 7.0), 5.84 (1H, m), 5.90 (1H, m), 5.92 (1H, d, 12.3), 5.96 (1H, dd, 12.3, 2.0), 13A: δ 1.99 (3H, d, 1.8), 2.16 (3H, d, 1.6), 4.62 (1H, m), 4.89 (1H, dm, 7.7), 5.80 (1H, m), 6.14 (1H, dm, 7.7), 13B: δ 1.51 (3H, s), 1.94 (3H, d, 1.9), 4.76 (1H, m), 5.86 (1H, dd, 10.9, 2.1), 6.36 (1H, m), 6.70 (1H, d, 10.9), 14Aa: δ 1.0-3.0 (18H, m), 4.79 (1H, dm, 1.6), 4.90 (1H, ddd, 8.2, 2.3, 1.5), 5.84 (1H, m), 6.17 (1H, dq, 8.2, 1.6), 14Ba: δ 1.0-2.6 (18H, m), 4.77 (1H, m), 5.80 (1H, dd, 10.4, 2.5), 6.66 (1H, d, 10.4), 6.75 (1H, m), 14Ab: δ 1.0-3.0 (14H, m), 4.93 (1H, m), 4.93 (1H, dt, 8.5, 1.6), 5.93 (1H, m), 6.18 (1H, ddt, 8.5, 1.8, 1.0).

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11) Synthesized in an analogous route to 3. Colorless oil, m/e 134 (M^+), 106 (M^+-CO), ν 1638, 1566 cm^{-1}(s), λmax 212 (log ϵ 4.13), 228 (4.25), 287 (3.66 sh), 300 (3.73), 312 nm (3.69 sh), λmax (50% H_2SO_4) 240 (log ϵ 4.72), 316 nm (4.09), δ (PMR) 2.28 (6H, brs), 6.77 (1H, m), 6.87 (1H, m), 6.91 (2H, m), δ (CF_3CO_2H) 2.87 (1H, s), 2.92 (1H, s), 8.12 (1H, dd, 12.2, 3.2), 8.14(1H, br.s), 8.27 (1H, br.s), 8.36 (1H, dd, 12.0, 2.0), δ (CMR) 26.9 (q), 27.5 (q), 136.6 (d, C_2), 138.9 (d, C_4), 139.2 (d, C_6), 140.8 (d, C_7), 143.5 (d, C_5), 147.7 (s, C_3), 186.4 (s, C_1), δ (CF_3CO_2H) 27.7 (q), 29.1 (q), 137.4 (d, C_2), 138.5 (d, C_7), 147.6 (d, C_4), 151.2 (d, C_6), 158.8 (s, C_5), 165.7 (s, C_3), 181.1 (s, C_1).

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