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DISTORTED TROPONES——[3]- AND [4](2,7)TROPONOPHANES WITH AN EXTRA ETHANO BRIDGE

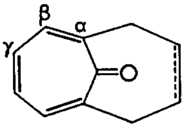
Yutaka Fujise, Yasuhiro Mazaki, Toshihiro Shiokawa, Yoshimasa Fukazawa and Shô Itô

Department of Chemistry, Tohoku University

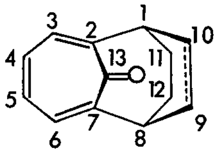
Sendai 980, Japan

Abstract: Four distorted tropones with bicyclic bridges were synthesized and their structures and physical properties investigated. They represent most distorted examples of tropone and exhibit abnormalities in various spectra and the decarbonylation reaction.

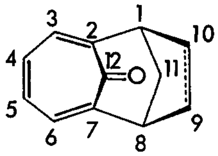
In the previous paper, we have reported the synthesis and some physical properties of [4]troponophane (1) and its dehydro compound 2[1)]. In the continued effort to understand the nature of strained tropone ring, we have synthesized tropones with double stranded bridges, i.e., tricyclo[6.2.2.$1^{2,7}$]trideca-2,4,6-trien-13-one (3) and -2,4,6,9-tetraen-13-one (4), tricyclo[6.2.1.$1^{2,7}$]dodeca-2,4,6-trien-12-one (5) and -2,4,6,9-tetraen-12-one (6), which represent the most distorted tropones hitherto known and exhibit abnormal spectral properties.



1: without F
2: with F

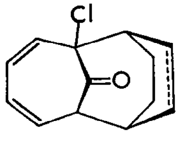


3: without F
4: with F

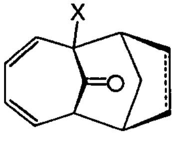


5: without F
6: with F

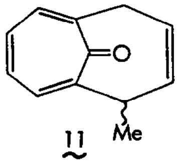
Synthesis Dehydrochlorination by base of the [6+4] adducts of 2-chlorotropone was employed. Thus, the reaction of the 2-chlorotropone-cyclohexadiene adduct 7[2)] with KOtBu in THF at -78° yielded 4 in 68% yield[3)]. The similar reaction of the 2-chlorotropone-cyclopentadiene adduct 8[4)] afforded 6 with correct spectral properties[3)], though too unstable to be isolated. The saturated phanes, 3 and 5, were obtained similarly from 9 and 10 (85% and 83% yield, respectively), prepared by respective diimide reduction of 7 and 8 (38% and 83% yield).



7: with F
9: without F



8: X=Cl, with F
10: X=Cl, without F



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Geometries of 3 and 5 Geometry and molecular dimensions of 3 were established by X-ray crystallography[5] as shown in Fig. 1. Major difference in the dimensions of the tropone rings in 3 (Fig. 1a) and in 1[1] is that interior bond angles at carbonyl and bridge head carbons are narrower in the former by 3° and 6°, respectively, than in the latter, suggesting deeper bent of the ring system in 3. This is clearly shown in the side view (Fig. 1b) with the bending angle as large as 71.1°. Fig. 1b also shows that the carbonyl group tilted inward contrary to the outward bending in 1[1].

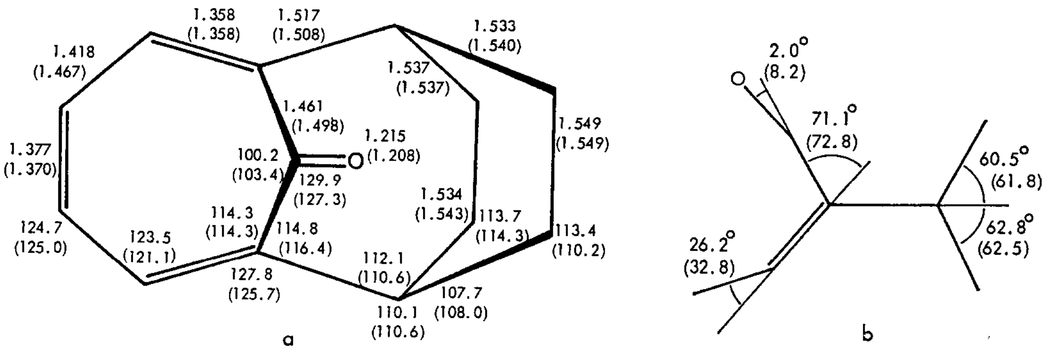


Fig. 1 Molecular dimensions (a) and side view (b) of 3 determined by X-ray analysis (figures without parentheses) and molecular mechanic calculations (figures in parentheses)

Since 5 decomposes upon X-ray irradiation, molecular mechanics calculations (MMPI)[6] were performed in order to visualize its geometry, estimate internal strain therein, and compare them with those of 3. The result on 3 (Fig. 1) is in agreement with the X-ray data, including bending of tropone ring and inward tilting of the carbonyl group, though exaggerated to some extent. Calculations on 5 (Fig. 2) disclosed even deeper bending of tropone ring than in 3. Total steric energies of 5 (63.1 kcal/mol) and 3 (61.8 kcal/mol) are 16-18 kcal/mol greater than that of 1. The excess steric energy in 3 and 5 is mainly originated from the tortional energy around the bridge-head double bonds, as is shown in Fig. 2c for 5.

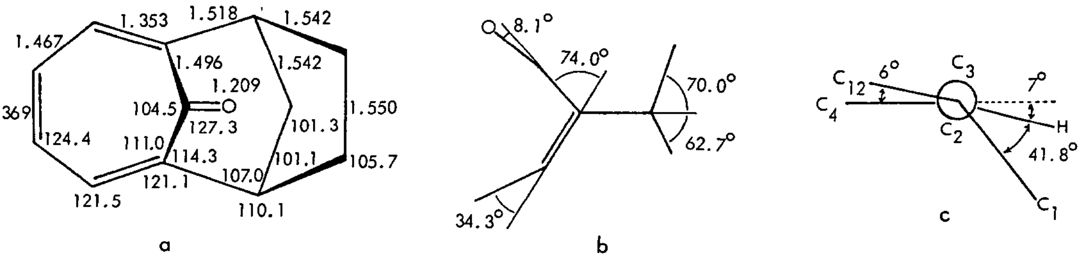


Fig. 2 Molecular dimensions (a) and side view (b) of 5 estimated by molecular mechanics calculations. c: Newman projection through the bridge-head double bond (C_2=C_3)

NMR spectra The geometries of 3 and 5 disclosed above imply that conjugation of the carbonyl group with the triene system is reduced in the order of 1, 3 and 5. This is verified by the chemical shift of protons and carbons in their tropone rings listed in Table. H_β and C_β shift up-field and $C_{c=o}$ down-field regularly on going from 1 through 3 to 5, while H_γ and C_γ remain nearly constant[7,8], being in accord with the general trend in the reduced conjugation[1].

Table PMR and CMR chemical shift of tropone ring in 1, 3 and 5

Compds	H_β	H_γ	C_α	C_β	C_γ	$C_{c=o}$
1	6.21	6.70	133.2	118.3	129.0	203.7
3	6.07	6.82	126.7	116.5	131.2	210.1
5	6.04	6.69	142.7	114.3	130.3	214.0

IR and Mass spectra and thermal decarbonylation The reduced conjugation and decrease of the carbonyl angle are reflected also in carbonyl frequency; ν: 1740 cm^{-1} for 3 and 1748 cm^{-1} for 5. The presence of double bond has a little effect (ν: 1745 cm^{-1} for 4). Molecular ions of 3, 4, 6 are observed only under mild conditions (10 eV. 40°C), but even then $[M^+-CO]$ peak appears as base peak. Thermal decarbonylation takes place at very low temperatures (115°C for 3, 94°C for 4, 80°C for 5, compared with 200°C for 1) to give smoothly the corresponding tricyclic benzene derivatives.

Electronic spectra Contrary to the electronic spectrum of 1, which shows only very weak $n-\pi^*$ transition, the spectra of 3 and 5 exhibit fairly strong absorptions at 316 nm for 3 and 324 nm for 5 which are $n-\pi^*$ in character as are verified by the solvent shift[3] (Fig. 3). Since larger the bent of tropone ring, stronger the absorption and longer the wave length, and further the introduction of double bond (3→4) causes practically no change in the spectrum, the origin of these unusually strong absorptions in such long wave lengths is believed to be due to the interaction of nonbonded orbital on the oxygen with the orbitals of triene system in bent tropone. In fact, modified version[9] of CNDO/S MO calculations revealed sizable transition between HOMO, and LUMO and nLUMO shown below.

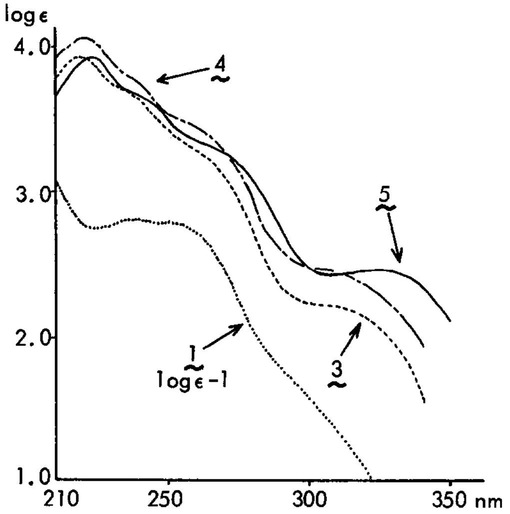
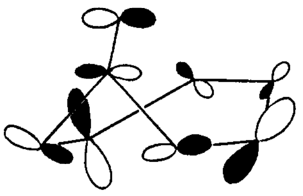
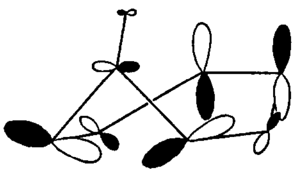


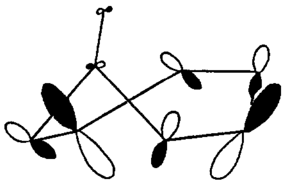
Fig. 3 Electronic spectra of troponophanes



HOMO
(-8.624 eV)



LUMO
(-1.306 eV)



nLUMO
(-0.896 eV)

References and Notes

1) Y. Fujise, T. Shiokawa, Y. Mazaki, Y. Fukazawa, M. Fujii and S. Itô, *Tetrahedron Letters*, **23**, 1601 (1982).

2) Prepared in 58% yield by heating 2-chlorotropone with 1,3-cyclohexadiene at 100°C for 9 hrs.

3) New compounds appeared in this paper have the following properties in addition to those described in the text. IR spectra were measured in KBr disk and NMR in $CDCl_3$ solution.

   3: Colorless prisms, m.p. 116°C (decomp.); $\lambda_{max}^{c\text{-}hex}$: 219.5 (log ϵ 3.93), 238 (3.66, sh), 264 (3.23, sh), 316 nm (2.18, sh, shifts to 312 nm in CH_3CN); PMR δ: 0.78 (2H, m), 1.67 (4H, m), 2.08 (2H, m), $J_{3,4}$ 5.62, $J_{4,5}$ 10.49, $J_{3,5}$ -0.48, $J_{3,6}$ 1.41; CMR δ: 29.6 (d), 26.7 (t), 22.8 (t).

   4: Colorless prisms, m.p. 94°C (decomp.); $\lambda_{max}^{c\text{-}hex}$: 220.5 (log ϵ 4.06), 239 (3.76, sh), 262 (3.42, sh), 311 nm (2.38, sh); PMR δ: 0.87 (2H, m), 1.63 (2H, m), 3.84 (2H, m), 6.22 (2H, m), 6.49 (2H, m), 6.88 (2H, m); CMR δ: 207.6 (s), 135.4 (d), 131.8 (d), 128.8 (s), 117.8 (d), 34.3 (d), 28.3 (t).

   5: Colorless prisms, m.p. 80°C (decomp.); $\lambda_{max}^{c\text{-}hex}$: 223 (log ϵ 3.93), 245 (3.61, sh), 271 (3.26, sh), 324 nm (2.47, shifts to 319 nm in CH_3CN); PMR δ: 1.57 (1H, dtt, 9.3, 2.4, 1.0), 1.86 (1H, dt, 9.3, 3.1), 1.95 (2H, m), 2.23 (2H, m), 3.26 (2H, br.ddd, 5.3, 3.1, 1.0), $J_{3,4}$ 5.33, $J_{4,5}$ 10.57, $J_{3,5}$ -0.74, $J_{3,6}$ 1.50; CMR δ: 69.2 (t), 46.7 (d), 26.8 (t).

   6: Unstable oil; ν_{CO}: 1715-1750 cm^{-1}; δ: 6.16 (m), 6.56 (m), 6.71 (m).

   7: Colorless prisms, m.p. 137.5-138.5°C; ν_{CO}: 1720 cm^{-1}; δ: 6.38 (2H, m), 6.02 (2H, m), 5.60 (2H, m), 3.77 (1H, t, 7.2), 3.11 (1H, m), 2.80 (1H, m), 1.1-2.3 (4H, m).

   9: Colorless prisms, m.p. 122-125°C; ν_{CO}: 1715 cm^{-1}; δ: 6.07 (2H, m), 5.65 (2H, m), 3.55 (1H, dd, 8.3, 5.7), 1.5-2.5 (10H, m).

   10: Colorless prisms, m.p. 86.5-87.5°C; ν_{CO}: 1723 cm^{-1}; δ: 5.4-5.9 (4H, m), 3.20 (1H, m), 2.40-2.83 (3H, m), 1.4-2.3 (5H, m).

4) S. Itô, K. Sakan and Y. Fujise, *Tetrahedron Letters*, 2873 (1970).

5) Compound **3** crystallizes from ether in orthorhombic prisms of space group $Pn2_1a$ with 4 molecules in a unit cell of dimensions a=12.955(2), b=10.121(2), c=7.318(1) Å. The structure was solved by MULTAN 78 and refined by block-diagonal least squares calculation. The final R value is 7.0%. Final crystallographic coordinates have been deposited in the Cambridge Crystallographic Data Center.

6) MMPI, QCPE=318, Indiana University (1983). N.L. Allinger and J.T. Sprague, *J. Am. Chem. Soc.*, **95**, 3893 (1973), N.L. Allinger, J.T. Sprague and T. Liljefors, *ibid.*, **96**, 5100 (1974).

7) The same trend is observed also between **4** (and partly **6**) and **2**. Cf. Ref. 1 and 3.

8) The down-field shift of C_α is partly ascribed to the substituent effect [-4.3 ppm, estimated from values of **2** and **11** (obtained from the 2-chlorotropone-piperylene adduct)]. The reason for the rest of the shift is unclear.

9) A. Tajiri, N. Ohmachi and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 2347 (1971). We thank Dr. Tajiri and Prof. Nakajima for their kind discussion.

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