[4] (2, 7) TROPONOPHANE

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Abstract: The title compound 5 and its dehydro analog 6 were synthesized from 10 and 9, respectively, and their physical properties were examined. Tropone ring in these compounds are deeply bent to tub shapes and conjugation of the carbonyl group is greatly reduced.

The smallest member of the [m]metacyclophane is 1 (m=5) described by Bickelhaupt¹⁾. Attempt to prepare [4]metacyclophane, the next lower homolog, resulted in the formation of the Dewar isomer 2^{2} . In the metatroponophane series, the smallest known bridge is C_6^{3} , although in the benzotroponophanes, tetramethylene compounds 3^{4} and 4^{5} have been prepared or recognized as reactive intermediates. We wish to report the synthesis and physical properties of [4](2,7)troponophanes 5 and its dehydro analog 6 which show extensively modified properties of tropone.



Synthesis Since the resulted troponophane is expected to suffer from internal strain, the routes involving migration of double bond at the crucial step were investigated. The carbon skeleton has been constructed by the [6+4] cycloaddition reaction of tropone and dienes; besides the known butadiene adduct $\frac{7^{6}}{7}$, acetoxy butadiene adduct 8 was obtained in 85% yield by heating two addends (84-90°, 5 days). Mild base treatment (KOH in EtOH) of 8 yielded tetraene 9 (80%), and diimide reduction afforded acetoxydiene 10.

Although the reaction of $RhCl_3 \cdot 3H_2O^{7}$ on 7 only gave tricyclic ketone 11 (19% yield), base treatment (KOtBu in tBuOH-THF, -78°) of 9 afforded a dark red solution, and subsequent acidification (-78°) furnished the desired troponophane 6 in 67% yield as colorless prisms, m.p. 94-95°. With the same base



(orange solution) and acid treatment of 10, [4](2,7)troponophane 5 was obtained in 56% yield as colorless prisms, m.p. 62–63°; 2,4–Dinitrophenylhydrazone, m.p. 184–185°. Spectral data and physical proper-

ties of these compounds are listed in Table⁸⁾.

<u>X ray Analysis</u> The crystal of 5 belongs to orthorhombic system of space group $P2_12_12_1$ with 4 molecules in a unit cell of dimensions <u>a</u>=10.705(2)Å, <u>b</u>=12.174(2), <u>c</u>=6.800(1). For analysis a total of 903 unique reflections was collected by CuKa radiation and the structure was solved by direct method. The final R value was 4.58%. The molecular dimensions are shown below⁹.



The tropone moiety bent 61.5° and 28.9° at C_1 and C_6 , and C_2 and C_5 , respectively, from the plane formed by these atoms to a tub conformation. These angles are larger than in tropylidene¹⁰⁾ and comparable with those in 3^{11} . Bond alternation in tropone moiety is more pronounced, the C=O bond length is shorter and bond angles are smaller than in tropone^{12,13)}. These structural features suggest the reduced conjugation in the tropone moiety, which is reflected in the following spectra.

<u>NMR Spectra</u> Tropone hydrogens in 5 and 6 are analysed as AA'BB' (under irradiation of allylic Hs) and assigned in comparison with the spectra of the corresponding $6-2-d^{14}$. The bridge hydrogens of 5 appear as complex multiplets. Carbons are assigned by specific decoupling of hydrogens.

Comparison of the PMR and CMR chemical shifts with the related compounds revealed the following remarkable features (Fig. 2). On going from the open chain tropone 12 to the short bridge troponophanes 5 and 6 through the longer bridge troponophanes 13^{15} and 14^{3} , there are regular changes both in hydrogens and carbons. β -H and β -C, as well as a-C show up-field shifts, and carbonyl carbons down-field shifts, while γ -H and γ -C shift a little. As the result β -H and β -C in 5 and 6 appear at higher fields than the γ -counterparts, the situation being very similar to those of 1,6-dimethyltropylidene 17 and the bridged compounds 15 and 16¹⁶.

Coupling constants of tropone hydrogens in 5 and 6 (Table) are also very similar to those of tropylidene¹⁷⁾ and different from those of tropone¹⁸⁾. These observations indicate the strong bond alternation in tropone ring and the reduced conjugation between carbonyl group and triene part.

<u>Electronic Spectra</u> Spectra of 5 and 6 (Fig. 3) are almost superimposable and the position of strong peaks at 250-260 nm corresponds to that of 15 (257 nm)¹⁶). The strong band at \sim 310 nm of the planar tropones 12 and 13¹⁵ is reduced to weak shoulder in 5 and 6, again showing the reduced conjugation between carbonyl group and triene.

IR Spectra, Mass Spectra and Decarbonylation as is expected from the narrow carbonyl angle. Both 5 and 6 exhibit carbonyl absorption at 1718 cm⁻¹,





Mass spectra of 5 and 6 show base peaks correspond to $[M-CO]^+$ along with small M^+ peaks (1.5% for 5, 0.7% for 6 at 8.3 eV, $30^{\circ}C$). Tetralin and 1,4-dihydronaphthalene were formed respectively on heating them at 200° , the temperature considerably lower than that (500°) required for the decarbonylation of tropone¹⁹. Thus, angular strain of the carbonyl group in 5 and 6 was manifested.

Stability of 5 and 6 as well as 3 compared with 4 is most probably due to the lack of double bond character in the C_1-C_{11} bond.



References and Notes

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TABLE Physical properties of new compounds

- $\sum_{n=1}^{5} \lambda_{n=2}^{n=hex} : 238 \text{ (log } \epsilon \text{ 3.81), } 247 \text{ nm } (3.79); v_{co}: 1718 \text{ cm}^{-1}; \text{ PMR } \delta_{8(9)}: 1.36, 1.79, \delta_{7(10)}: 2.26, 2.68 \text{ (each complex m), } \delta_{2(5)}: 6.21, \delta_{3(4)}: 6.70 \text{ ppm, } J_{2,3}: 5.36, J_{2,4}: 0.37, J_{2,5}: 0.66, J_{3,4}: 10.98 \text{ Hz; CMR } \delta_{1(6)}: 133.2, \delta_{2(5)}: 118.3, \delta_{3(4)}: 129.0, \delta_{7(10)}: 29.3, \delta_{8(9)}: 25.8, \delta_{11}: 203.7 \text{ ppm.}$
- 6, $\lambda_{max}^{c-hex} : \overline{236} (\log \epsilon \ 3.75), \overline{250} \text{ nm} (3.74); \nu_{co} : 1718 \text{ cm}^{-1}; \text{ PMR } \delta_{2(5)} : 6.29, \delta_{3(4)} : 6.83, \delta_{7(10)} : 3.02, \delta_{7'(10')} : 3.42, \delta_{8(9)} : 5.66, J_{2,3} : 5.66, J_{2,4} : -0.05, J_{2,5} : 0.70, J_{3,4} : 11.06, J_{5,7} : 1.0, J_{7,7'} : 15.3, J_{7',8} : 2.5, J_{7',9} : 1.0; \text{ CMR } \delta_{1(6)} : 126.3, \delta_{2(5)} : 118.2, \delta_{3(4)} : 129.0, \delta_{7(10)} : 31.3, \delta_{8(9)} : 123.2, \delta_{11} : 202.8 \text{ ppm}.$
- 8 colorless plates, m.p. 42-45.5°; m/e 218 (M⁺), 107 (b.p.); λ max: 244 (log ϵ 3.25, sh), 252 (3.27), 258 (3.19, sh), 293 nm (2.27); v: 1725, 1680, 1370, 1235 cm⁻¹; δ : 2.05 (3H, s), 2.53 (2H, m), 3.51 (1H, m), 3.66 (1H, dt, J: 2.0, 6.5), 5.5-6.08 (7H, m).
- 2 yellow prisms, m.p. 49-50°; m/e: 158 (M⁺), 157 (M⁺-1, b.p.); λ max: 232 (log ε 3.95), 330 nm (3.47); δ:
 2.22 (1H, dtd, J: 14, 7, 2), 3.14 (1H, dddt, J: 12, 5, 1), 3.50 (1H, ddd, J: 12, 7, 5), 5.48-6.23 ppm (7H, m).
- 10 colorless prisms, $67.5-69^{\circ}$; m/e: 220 (M⁺), 107 (b.p.); λ max: 249 (log ϵ 3.70), 288 nm (2.63); v: 1725, 1690, 1235 cm⁻¹; δ 1.50-2.0 (6H, m), 1.99 (3H, s), 3.29 (1H, br.dd, J: 11, 5), 3.49 (1H, br.t, J: 8), 5.06 (1H, br.td, J: 7, 4), 5.67 (2H, m), 6.03, 6.05 (each 1H, m).
- colorless oil; m/e: 160 (M⁺), 91 (b.p.); λmax: 298 nm (log ε 2.09), ν^{oil}: 1712 cm⁻¹, δ: 1.6-2.3 (4H),
 2.32-2.67 (2H, m), 2.82 (1H, m), 3.20 (1H, br.dd, J:8, 6), 5.47 (1H, br.dd, J:12, 4), 5.80 (1H, dd, J: 12, 8), 6.03 (1H, br.ddd, J:10, 7, 1), 6.40 ppm (1H, br.ddd, J:10, 6, 1).
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