Synthesis and Spectroscopic Characterisation of 4-Chloro-[6](3,5)-Troponophane

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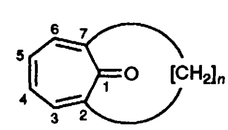
Treatment of the tricyclic enone **4d** with perchloric acid results in the formation of the title troponophane **3d** which contains the shortest (3,5)-polymethylene bridge reported to date.

Unlike their [*n*](2,7)-counterparts **1**,[1] short-bridged ($n \leqslant 6$) [*n*](2,4)- and [*n*](3,5)-troponophanes (**2** and **3**, respectively) remain unknown.[2,3] Since 7-halogenobicyclo[4.1.0]hept-4-en-3-ones are generally excellent precursors to troponoids,[4] [*n*.4.1]propellenones of the type **4** might be expected to undergo ring-expansion and accompanying dehydrohalogenation to give the corresponding [*n*](3,5)-troponophane **3**. We have embarked on a programme aimed at pursuing such possibilities, and our previous studies[4b] have established that compounds **4a** and **b** are completely stable entities that do not undergo the desired ring-expansion process. In contrast, the next higher homologue, **4c**, proved to be unstable[5] and, on standing at room temperature, engaged in novel rearrangement processes which were suggestive of the intermediacy of the '*meta*'-bridged tropylium ion **5**, the conjugate acid of troponophane **3c**. However, despite various efforts, **3c** could not be isolated from any of the reaction mixtures. These difficulties are undoubtedly a manifestation of the highly strained nature of **3c**, so attention was turned to the preparation of the less strained homologue **3d**. We now report that treatment of propellenone **4d** with mineral acid results in the production of the title troponophane **3d** which can be isolated and characterised spectroscopically.

The synthesis of the [6.4.1]propellenone **4d** (Scheme 1) involved Birch reduction of the cyclooctane **6**[6] as the first step. The resulting *ca.* 1:7 mixture of products **7**[7] and **8**[8] was subjected to reaction with ethyl trichloroacetate–sodium methoxide and the corresponding mixture of dichlorocarbene adducts, **9**† (*ca.* 7% from **6**, mp 35.5–36.5 °C) and **10** (75%, mp 87–88 °C), could be separated from one another by fractional crystallisation. Epoxidation of alkene **10** was accomplished under standard conditions, but the resulting epoxide **11** (99%, mp 119–120 °C) could not be rearranged to the isomeric allylic alcohol on treatment with base. However, reaction of **11** with sodium phenylselenide in refluxing *n*-butanol[9] resulted in clean formation of the hydroxyselenide **12** (82%, mp 137.5–138.5 °C) which when treated with sodium metaperiodate produced the allylic alcohol **13** (88%, mp 96–98 °C). Finally, oxidation of compound **13** with pyridinium chlorochromate (PCC) resulted in the formation of the target enone **4d** (85%), which was characterised by ^{13}C and ^{1}H NMR spectroscopy.‡



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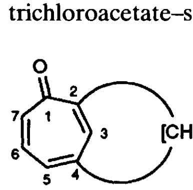

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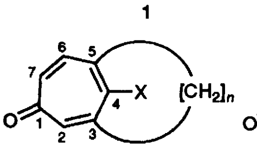
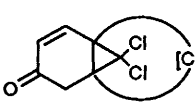
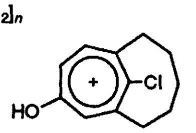


3a; $n = 3$, X = Cl
3b; $n = 4$, X = Cl
3c; $n = 5$, X = Cl
3d; $n = 6$, X = Cl



4a; $n = 3$
4b; $n = 4$
4c; $n = 5$
4d; $n = 6$



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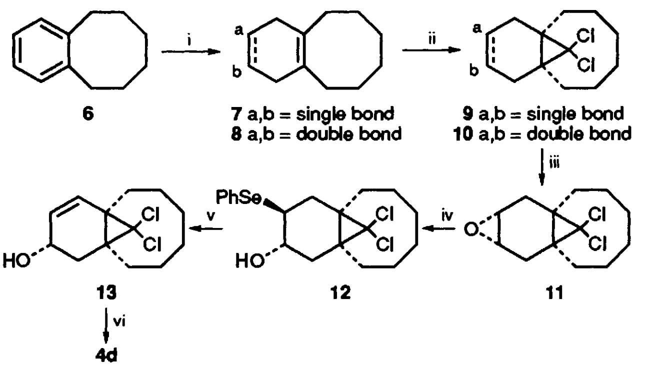

Scheme 1 *Reagents and conditions*: i, Na, NH_3, EtOH, Et_2O, −78 °C, 5 h; ii, Cl_3CCO_2Et (2 equiv.), NaOMe (3 equiv.), pentane, 0 °C, 3 h; iii, *m*-$ClC_6H_4CO_3H$ (1.1 equiv.), CH_2Cl_2, 18 °C, 4 h; iv, PhSeNa (2 equiv.), Bu^{n}OH, 118 °C, 23 h; v, $NaIO_4$ (2 equiv.), THF, 66 °C, 5 h; vi, PCC (4 equiv.), NaOAc, CH_2Cl_2, 18 °C, 0.5 h

Propellenone **4d** proved to be a very unstable species which decomposed rapidly both in solution and in the solid state. However, treatment of a *ca.* 0.4 mol dm^{-3} chloroform solution of this compound with 4 equiv. of 70% aq. perchloric acid resulted in its rapid (1 h at 18 °C) conversion into the target troponophane **3d**‡ [54%, mp 66–70 °C (decomp.)] which could be isolated by flash chromatography[10] on silica gel (R_f 0.5 in 5:95 Et_2O–CH_2Cl_2). The ^{1}H NMR spectrum‡ of compound **3d** possessed features strongly suggestive of the presence of a phane system. Thus, the one-proton multiplet at δ 0.00 is assigned to a proton associated with the central carbons (Cγ/Cγ′) of the hexamethylene bridge and which is forced to project into the shielding zone of the troponoid ring. In addition, the chemical shifts (δ *ca.* 3.0) and multiplicities of the signals due to two of the protons attached to Cα and/or Cα′ are very similar to those reported for the analogous protons in 13-bromo[7]-metacyclophane[11] and [7](3,7)-tropolonophane.[12] In an effort to provide more support for the structure **3d**, spectral comparisons were made with the model compound **14**‡ (readily prepared by established methods[13] from *o*-xylene). The low field regions in the ^{13}C NMR spectra of these two compounds were very similar. In the ^{1}H NMR spectra, signal multiplicities and coupling constants for the troponoid ring protons were essentially identical (Table 1), but the chemical shifts of the signals due to the protons in **3d** were shielded with respect to their counterparts in **14**. This shielding is most pronounced for H(2) and H(7) but the precise origins of these effects remain unclear at present.

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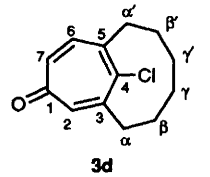

3d

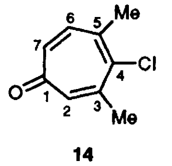

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Table 1 Comparison of selected ^{1}H NMR spectral parameters (δ, J/Hz) for compounds **3d** and **14**^{a}

	H(2)	H(6)	H(7)	$J_{6,7}/J_{7,6}$	$J_{2,7}/J_{7,2}$
14	6.85	6.03	6.63	12.2	2.7
3d	6.13	5.97	6.41	12.0	2.7
Δδ	−0.72	−0.06	−0.22	—	—

^{a} Spectral data acquired in C_6D_6 solution at 21.2 °C.

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Footnotes

† All new compounds had spectroscopic data [IR, UV (where appropriate), NMR, mass spectrum] consistent with the assigned structure. Satisfactory combustion and/or high resolution mass spectral analytical data were obtained for all new compounds except **4d**. Reported yields refer to isolated materials.

‡ *Selected spectral data* for **4d**; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 147.8, 131.2, 35.5, 34.6, 29.1, 28.9, 26.3, 25.9, 25.7 and 25.0 [signals due to C(11) and C(4a) or C(10a) obscured]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 [d, *J* 9.8 Hz, 1H, H(4)], 6.18 [d, *J*, 9.8 Hz, 1H, H(3)], 2.61 [s, 2H, H(1)], 2.17 (dt, *J* 15, 4 Hz, 1H), 1.87 (dt, *J* 15, 3.5 Hz, 1H), 1.79 (m, 1H), 1.75–1.25 (complex m, 9H).

Selected spectral data for **3d**; ^{13}C NMR (100 MHz, C_6H_6) δ 187.1 (C), 147.6 (C), 141.9 (C), 139.5 (C), 136.4 (CH), 135.5 (CH), 129.5 (CH), 37.2 (CH_2), 34.1 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 25.8 (CH_2), 25.4 (CH_2); ^{1}H NMR (400 MHz, C_6H_6) δ 6.41 [dd, *J* 12.0, 2.7 Hz, 1H, H(7)] 6.13 [d, *J* 2.7 Hz, 1H, H(2)], 5.97 [(d, *J* 12.0 Hz, 1H, H(6)], 3.07 (ddd, *J* 12.8, 12.7, 5.9 Hz, 1H), 2.97 (m, 1H), 1.88 (ddd, *J* 12.7, 5.4, 2.7 Hz, 1H), 1.82 (m, 1H), 1.49 (m, 1H), 1.37 (m, 1H), 1.24–1.08 (complex m, 4H), 0.74 (m, 1H), 0.00 (m, 1H); MS *m/z* (EI, 70 eV) 225 (5%) 223 (16) [$M + H^+$], 224 (6), 222 (14) [M^+], 196 (4), 194 (12) [$M - CO^+$], 187 (12) [$M - Cl^+$], 159 (100) [$M - CO - Cl^+$]; ν_{max} 1637 cm^{-1}; λ_{max} ($CHCl_3$) 239 (log ε 4.00), 260 (sh, 3.85), 350 (3.69) nm; HRMS, M^+ *m/z* 222.0808. $C_{13}H_{15}{}^{35}ClO$ requires M^+ 222.0811.

Selected spectral data for **14**; ^{13}C NMR (100 MHz, C_6H_6) δ 184.7 (C), 144.3 (C), 140.9 (C), 139.9 (C), 139.1 (CH), 138.6 (CH), 137.4 (CH), 28.1 (CH_3), 26.8 (CH_3); ^{1}H NMR (400 MHz, C_6H_6) δ 6.85 [br s, 1H, H(2)], 6.63 [dd, *J* 12.2, 2.7 Hz, 1H, H(7)], 6.03 [d, *J* 12.2 Hz, 1H, H(6)], 1.83 (d, *J* 1.0 Hz, 3H, CH_3), 1.76 (s, 3H, CH_3); ν_{max} (KBr) 1624, 1591, 1555 cm^{-1}; λ_{max} ($CHCl_3$) 242 (log ε 4.29), 313 (sh, 3.90), 321 (3.94) nm.

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