Synthesis and Valence Isomerization of Alkylated Thia[11]annulenes†

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Summary The synthesis of the alkylated mono-*trans*-thia[11]annulenes (4a) and (4b) is described, which readily undergo valence isomerization to the dihydrobenzo-thiepins (5a) and (5b).

FULLY unsaturated large ring monoheterocycles (hetero-annulenes) are an interesting class of compounds, which, until recently have been little studied. In the 11-membered ring series, a benzo-fused thia[11]annulene[1] as well as bridged thia- and oxa-[11]annulenes[2] have previously been synthesized. It was of interest to prepare a hetero[11]-annulene not containing a fused aromatic ring or a bridging group, in order to find out whether it behaves as a 12π-electron system, and whether it undergoes ready valence isomerization as do [10]-[3,4] and [12]-annulene.[5] We now report the realization of this objective, namely the synthesis of the alkylated mono-*trans*-thia[11]annulenes (4a) and (4b). The ready valence isomerization of these substances prevented their isolation, and their presence could be detected only by n.m.r. spectrometry.

† For previous paper in the series, 'Unsaturated Macrocyclic Compounds,' see B. W. Metcalf and F. Sondheimer, *J. Amer. Chem. Soc.*, in the press.

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Wittig reaction of the dialdehyde (1)[6] and the dichloride (2)[7] in dimethylformamide with ethanolic lithium ethoxide at 90°[8] led to 5·3% of the furan-fused mono-*trans*-thia[11]-annulene (3) (isolated by chromatography on alumina), as colourless crystals, m.p. 125·5—127°;‡ m/e 310; λ_{max} (cyclohexane) 226 (ϵ 24,200), ca. 238sh (23,400), 280 (14,000), and ca. 300sh nm (11,400); ν_{max} (KBr) 985(s) cm^{-1} (*trans*-olefin). The structure and stereochemistry of (3) were confirmed by the n.m.r. spectrum (CCl$_4$; 100 MHz); τ 2·73(s) and 2·78(s) (12-H, 14-H), 2·95 and 3·86 (ABq, 4-H, 5-H, $J_{4,5}$ 16·5 Hz), 3·40 and 3·56 (ABq, 8-H, 9-H, $J_{8,9}$ 12 Hz), and 7·40—8·80 (broad m, CH$_2$). Further support for structure (3) was obtained by catalytic hydrogenation
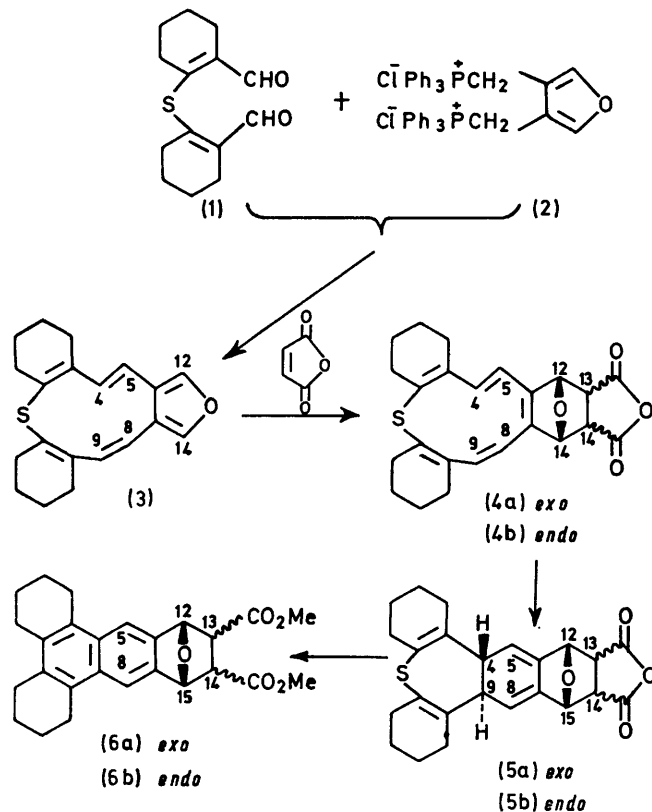
(EtOAc, 10% Pd–C) to the corresponding 4,5,8,9-tetra-hydro-derivative, and by desulphurization (EtOAc, Raney nickel, H$_2$) to 3,4-di-(β-cyclohexylethyl)furan, both these liquid products showing the expected spectral properties.

The furan ring in (3) could be modified by Diels-Alder reaction with various dienophiles, the most interesting results being obtained with maleic anhydride. Thus, treatment of (3) with 1·1 mol. equiv. of maleic anhydride in benzene at room temp. for 24 h, followed by removal of excess of reagent by sublimation (35° at 15 mmHg), led to

a ca. 2 : 1 mixture of the *exo*- and *endo*-dihydrobenzothiepins (5a) and (5b); m/e 408·147 (calcd. 408·140); λ_{max} (EtOH) 246 (ϵ 8100) and ca. 260sh nm (5000); ν_{max} (KBr) 1860(m) and 1775(s) cm^{-1} (anhydride). The n.m.r. spectrum (C$_6$D$_6$; 100 MHz) of (5a,b) showed bands at τ 4·55(s) and 4·92(s) [5-H, 8-H in (5b)], 4·68(s) and 4·78(s) [5-H, 8-H in (5a)], 4·94(s) and 5·00(s) [12-H, 15-H in (5a)], 5·15—5·34 [m, 12-H, 15-H in (5b)], 5·90 and 6·46 [ABq, 4-H, 9-H in (5a,b), $J_{4,9}$ 17 Hz], 6·85—6·97 [m, 13-H, 14-H in (5b)],§ 7·37 [s, 13-H, 14-H in (5a)],§ and 7·50—8·90 (m, CH$_2$).

The structures and stereochemistry assigned to (5a,b) are based mainly on an analysis of the n.m.r. spectrum, which indicated a mixture of two isomers being present in a ratio of ca. 2 : 1. These conclusions were confirmed through the conversion of (5a,b) to a ca. 2 : 1 mixture of the naphthalenes (6a) and (6b) (separated by preparative t.l.c.) through successive treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in boiling benzene,¶ followed by boiling in methanol and esterification with diazomethane. The *exo*-ester (6a) showed m.p. 255—257°;‡ m/e 420·193 (calcd. 420·194); main λ_{max} (cyclohexane) 247 nm (ϵ 99,000); ν_{max} (KBr) 1735(s) cm^{-1} (ester); τ (CDCl$_3$, 60 MHz), 2·17 (s, 5-H, 8-H), 4·21 (s, 12-H, 15-H), 6·27 (s, OMe), 6·99 (s, 13-H, 14-H),§ 6·75—7·50 (m, benzylic-CH$_2$), and 7·95—8·30 (m, nonbenzylic CH$_2$). The *endo*-ester (6b) showed m.p. 143—144°;‡ mass spectrum, m/e 420·193; main λ_{max} (cyclohexane) 246 nm (ϵ 108,000); ν_{max} (KBr) 1740(s) cm^{-1} (ester); τ(CDCl$_3$; 60 MHz), 2·12 (s, 5-H, 8-H), 4·30—4·45 (m, 12-H, 15-H), 6·25—6·35 (m, 13-H, 14-H),§ 6·57 (s, OMe), 6·75—7·45 (m, benzylic CH$_2$), and 7·95—8·25 (m, nonbenzylic CH$_2$).

The formation of (5a) and (5b) by the reaction of (3) with maleic anhydride presumably involved the mono-*trans*-thia[11]annulenes (4a) and (4b) as intermediates, and this could be confirmed by monitoring the reaction in [^{2}H$_6$]-benzene at room temperature by n.m.r. spectrometry (100 MHz). Signals due to (4a,b) could be detected after 5 min, and these reached their maximum intensity after ca. 30 min. [at this stage, bands due to (5a,b) were already present]. They then decreased, while bands due to (5a,b) increased, until after ca. 3 h essentially only the spectrum of (5a,b) was observable. The n.m.r. spectrum of (4a,b) was entirely in accord with the assigned structures [ca. 2 parts (4a), 1 part (4b)], showing the following absorptions: τ 3·23 [broad d, 4-H in (4a,b), $J_{4,5}$ 14 Hz], 3·70 [d, 9-H in (4b), $J_{9,8}$ 10 Hz], 3·87 [d, 9-H in (4a), $J_{9,8}$ 10 Hz], 3·99 [d, 8-H in (4a,b), $J_{8,9}$ 10 Hz], 4·19 [d, 5-H in (4b), $J_{5,4}$ 14 Hz], 4·34 [d, 5-H in (4a), $J_{8,9}$ 14 Hz], 4·95(s) and 5·05(s) [12-H, 15-H in (4a)], 5·12—5·30 [m, 12-H, 15-H in (4b)], 6·94—7·04 [m, 13-H, 14-H in (4b)],§ 7·41 [s, 13-H, 14-H in (4a)],§ and ca. 7·50—8·90 (CH$_2$). It was not possible to determine other spectral data of (4a,b), since appreciable amounts of (3) or (5a,b) were always present.

The n.m.r. spectrum of (4a,b) indicates no appreciable paramagnetic ring current effect, in contrast to carbocyclic 12π-electron systems,[5,10] and the macrocyclic ring is pre-

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‡ Satisfactory elemental analyses were obtained for all new crystalline compounds.

§ The assignment of the singlet 13-H, 14-H resonances in the n.m.r. spectra of (4a,b), (5a,b) and (6a,b) to the *exo* isomers, and the multiplet 13-H, 14-H resonances to the *endo*-isomers, is based on the observed multiplicities of the corresponding proton resonances in the *exo*- and *endo*-adducts of furan with maleic anhydride (see ref. 9).

¶ The DDQ treatment results in dehydrogenation and loss of sulphur, the intermediate presumably being the corresponding benzothiepins [(5a,b), double bond at $\Delta^{4(9)}$]. This type of benzothiepin could in fact be isolated when the adduct from (3) and dimethyl fumarate was dehydrogenated with DDQ in benzene at room temperature, and was shown to give the corresponding naphthalene by loss of sulphur on standing in solution.

sumably nonplanar. The effect of passing from a benzo- or furo-thia[11]annulene to an alkylated derivative therefore does not increase the tendency of the 11-membered ring to become planar, but merely reduces the thermal stability of the molecule. The disrotatory thermal valence isomerization of (4a,b) to (5a,b) is in accord with orbital symmetry considerations,[11] and is analogous to the thermal isomerization of mono-*trans*-[10]annulene to *trans*-9,10-dihydronaphthalene.[4]

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