Cycloaddition of the Anion derived from Homophthalic Anhydride to *cis,cisoid,cis*-Tricyclo[6.3.0.0^{2,6}]undeca-4,9-diene-3,11-dione. Aromatization as a Driving Force for Intramolecular Sigmatropic Hydrogen Transfer

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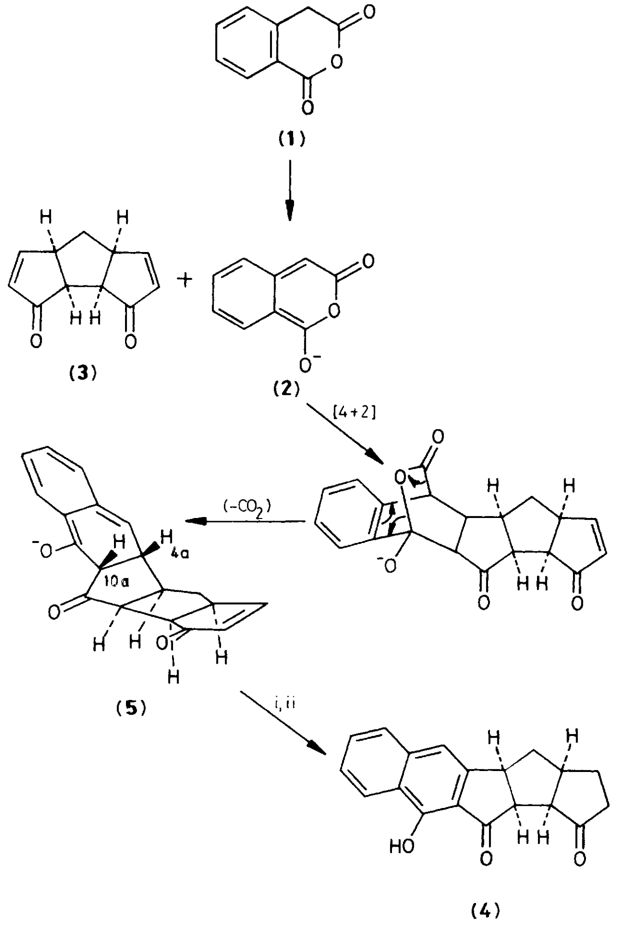
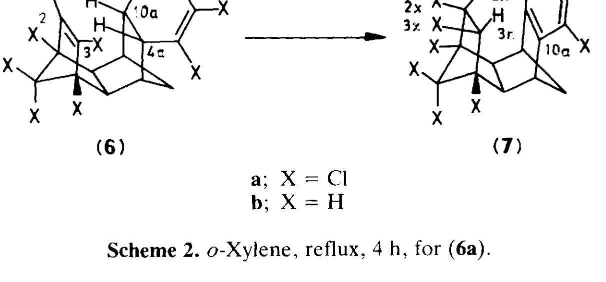
Reaction of the anion derived from homophthalic anhydride with *cis,cisoid,cis*-tricyclo[6.3.0.0^{2,6}]undeca-4,9-diene-3,11-dione proceeds *via* initial Diels–Alder cycloaddition followed by intramolecular dyotropic hydrogen migration with concomitant aromatization; the structure of the reaction product (**4**) (formed in 42% yield) was established *via* single-crystal *X*-ray structural analysis.

As part of a programme that involves the construction of potential new molecular host systems,[1] we have investigated the thermal reaction of the anion (**2**) [derived from homophthalic anhydride[2—4] (**1**)] with *cis,cisoid,cis*-tricyclo-[6.3.0.0^{2,6}]undeca-4,9-diene-3,11-dione (**3**). Thus, a mixture of (**1**), sodium hydride, and dienophile (**3**)[5] (1 equiv.) was heated in anhydrous toluene at 150 °C (sealed tube) for 12 h. The mixture was quenched by addition of aqueous ammonium chloride. Work-up afforded a 1:1 cycloadduct (**4**) in 42% yield (Scheme 1). Analysis of the ^{1}H and ^{13}C n.m.r. spectra of (**4**) clearly indicated the presence of: (i) a 2,3-disubstituted-1-naphthol moiety and (ii) a substituted cyclopentanone moiety.† Unequivocal proof of the structure of (**4**) was secured *via* single-crystal *X*-ray analysis.‡ A drawing of the structure thereby obtained is shown in Figure 1.

Of particular interest is our observation that the Diels–Alder [4 + 2] cycloaddition of (**2**) to (**3**) is accompanied by intramolecular sigmatropic hydrogen transfer with concomitant aromatization of the Diels–Alder cycloadduct. Such dyotropic[6] (group transfer) rearrangements, which are symmetry-allowed thermal processes that involve concerted rupture of two carbon–hydrogen σ-bonds, have been observed infrequently in other, suitably constructed polycyclic systems.[7—13] In some cases, aromatization contributes to the overall driving force for dyotropic hydrogen transfer. A



Scheme 1. i, Dyotropic hydrogen migration; ii, aqueous acidic work-up.



a; X = Cl
b; X = H

Scheme 2. *o*-Xylene, reflux, 4 h, for (**6a**).

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† *Spectral data* for (**4**): i.r. (KBr) 3300s, 1730s, 1670s, 1620s, 1570m cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 0.77—1.06 (m, 2H), 2.03—2.28 (m, 1H), 2.48—2.74 (m, 1H), 2.76—3.15 (m, 1H), 3.41—3.73 (m, 1H), 3.84—4.36 (m, 1H), 7.23 (s, 1H), 7.34—8.39 (m, 4H), 10.13 (br. s, 1 H); ^{13}C n.m.r. (CDCl$_3$) δ 25.79 (t), 37.19 (t), 37.40 (t), 45.82 (2C, d), 55.70 (d), 55.98 (d), 114.31 (d), 115.53 (s), 122.93 (s), 123.82 (s), 124.95 (d), 127.55 (d), 129.76 (d), 139.35 (s), 149.90 (s), 155.84 (s), 208.50 (s), 217.00 (s). Satisfactory elemental analyses were obtained.

‡ *Crystal data* for (**4**) (a single crystal, m.p. 183—184 °C, obtained *via* fractional recrystallization from ethyl acetate–hexane): $C_{19}H_{16}O_3$, M = 292.3, orthorhombic, space group *Pbca*, a = 7.578(a), b = 12.503(2), c = 29.263(4) Å, U = 2773.9(5) Å^3, D_c = 1.410 g cm^{-3}, μ = 0.88 cm^{-1}, $F(000)$ = 1232, Z = 8. Diffraction intensities were measured on a Nicolet P2$_1$ diffractometer with graphite monochromatized Mo-K_α (λ = 0.71073 Å) radiation, Wyckoff mode ($3 \leqslant 2\theta \leqslant 45°$, 2θ fixed ω varied), variable scan rate (4—29.3 degrees min^{-1}), using a crystal with dimensions 0.18 × 0.23 × 0.43 mm. A total of 1277 reflections were collected at room temperature. Block-cascade least-squares refinement was employed. H-atoms were refined isotropically; all others were refined anisotropically. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized with $w = [\sigma^2(F_o) + 0.00023\,F_o^2]^{-1}$. The final R index was 0.0468, R_w was 0.0422 for 1277 reflections [$I \geqslant 3\sigma(I)$] and 264 parameters, S = 1.298, $(\Delta/\sigma)_{max}$ = 0.020, largest peaks in final difference map of 0.019 e Å^{-3}. Computer programs were supplied by Nicolet Instrument Corporation (1986) for Desktop 30 Microeclipse and Nova 4/c configuration. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Results of molecular mechanics calculations[14] for (**5**) → (**4**) and for (**6b**) → (**7b**).

	(**5**)	(**4**)	(**6b**)	(**7b**)
ΔH_f/kJ mol^{-1}	−113.6	−335.5	299.3	153.6
E_π/kJ mol^{-1}	86.6	294.6	12.3	160.7
E_{steric}/kJ mol^{-1}	179.9	165.6	261.4	266.2
E_{strain}/kJ mol^{-1}	162.5	147.6	231.0	236.4
d/Å[a]	H(4a)· · ·C(3), 3.02 H(10a)· · ·C(2), 4.47		H(8a)· · ·C(2), 2.43	H(2n)· · ·C(8a), 2.48

[a] Intramolecular distance for dyotropic hydrogen migration.

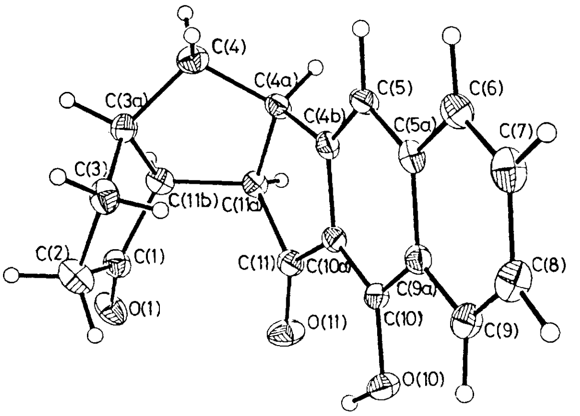

Figure 1. Structure of (**4**).

mechanism that accounts for the formation of (**4**) and that takes advantage of aromatization as a driving force for dyotropic hydrogen transfer is shown in Scheme 1.

It is instructive to compare our results with those reported earlier by Mackenzie[7] for the dyotropic hydrogen shift represented by (**6a**) → (**7a**) (Scheme 2). We have performed molecular mechanics calculations[14] on the (presumed) intermediate (**5**) (Scheme 1), and on the product (**4**) which results *via* dyotropic hydrogen migration in (**5**). We have also performed similar calculations on hydrocarbon analogues of (**6a**) and (**7a**) [*i.e.*, the corresponding dechloro compounds, (**6b**) and (**7b**) respectively]. The results of these calculations are shown in Table 1. Of particular significance is the fact that the relevant transannular nonbonded distances in (**5**) are considerably larger than those in (**6b**) and in (**7b**) [*i.e.*, 3.02 and 4.47 Å in (**5**) *vs.* 2.43 Å in (**6b**) and 2.48 Å in (**7b**)]. To our knowledge, the intramolecular distances that migrating hydrogen nuclei must traverse when undergoing the dyotropic hydrogen migration represented by (**5**) → (**4**) are the largest among such examples that have been reported thus far.[7—13] In this regard, it is particularly significant that dyotropic hydrogen migration in (**5**) takes place in good overall yield.

The data in Table 1 show that, in each example, no significant difference in steric and/or strain energy occurs as a result of dyotropic hydrogen migration [*i.e.*, the values of ΔE_{steric} and ΔE_{strain} for (**5**) → (**4**) and (**6b**) → (**7b**) are quite small]. Hence, we ascribe the driving force for each of these dyotropic hydrogen migrations to the gain in π-energy [ΔE_π = 208.0 and 148.4 kJ/mol for (**5**) → (**4**) and (**6b**) → (**7b**), respectively] that results from aromatization concomitant with rearrangement.

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