Photo-induced Transformations. Part 76.[1] Ring Expansion through a [2 +2] Photocycloaddition-β-Scission Sequence; the Photorearrangement of endo-4-Cyanotricyclo[6.4.0.0²·⁵]dodeca-1(12),6,8,10-tetraen-5-yl Hypoiodite to 4-Cyanotricyclo[6.4.0.0²·⁴]dodeca-1(12),6,8,10-tetraen-5-one.[2] X-Ray Crystal Structure of 4-Cyanotricyclo[6.4.0.0²·⁴]dodeca-1(12),6,8,10-tetraen-5-one

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The irradiation of endo-4-cyanotricyclo[6.4.0.0²·⁵]dodeca-1(12),6,8,10-tetraen-5-ol (1), derived from the [2 + 2] photocycloaddition of 2-naphthol with acrylonitrile, in the presence of HgO–I₂ in benzene, gives 4-cyanotricyclo[6.4.0.0²·⁴]dodeca-1(12),6,8,10-tetraen-5-one (2) in 40% yield. The unique molecular structure of product (2), which has the flattened boat conformation of a seven-membered ring, was determined by means of X-ray crystallographic analysis.

We reasoned that the combination of a mixed [2 + 2] photocycloaddition of an enolized ketone with an alkene[3] and the β-scission of an alkoxyl radical generated from the resulting cyclobutanol might lead to a ring enlargement and ought to be of value in organic synthesis.†

In order to prove the utility of this reaction sequence, we chose as a substrate 4-cyanotricyclo[6.4.0.0²·⁵]dodeca-1(12),-6,8,10-tetraen-5-ol (1), a cyclobutanol, prepared by means of the

can be expanded to form a 7-membered ring fused with a cyclopropane ring. We now report the results.

The cyclobutanol (1) was readily prepared according to the reported procedure.[4] Irradiation of photocycloadduct (1) in benzene containing mercury(II) oxide and iodine in a Pyrex vessel with a 100-W high-pressure Hg arc for 5 h under nitrogen gave a crystalline product (2) in 40% yield. The molecular formula of the product (2) was determined by elemental
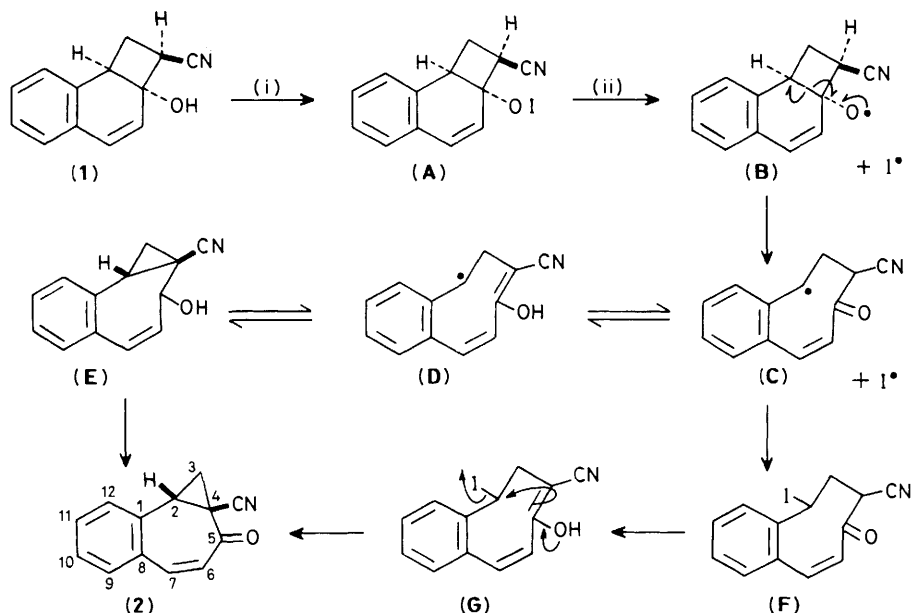
Scheme. *Reagents and conditions:* (i) HgO–I₂; (ii) hv

photocycloaddition of β-naphthol with acrylonitrile after the method of Akhtar and McCullough;[4]‡ we then investigated its photolysis in benzene in the presence of mercury(II) oxide–iodine, a proven reagent for the generation of a hypoiodite from an alcohol.[5] We found that a 6-membered ring of adduct (1)

analysis and mass spectrometry to be C₁₃H₉NO. The structure of product (2) was deduced to be 4-cyanotricyclo-[6.4.0.0²·⁴]dodeca-1(12),6,8,10-tetraen-5-one on the basis of the spectroscopic evidence (see Experimental section). This was then confirmed by an X-ray crystallographic analysis.

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† Another synthetic utilization of cyclobutanes obtained by photo-cycloaddition has recently been described: W. Oppolzer, *Acc. Chem. Res.*, 1982, **15**, 135.

‡ The stereochemistry of the adduct (1) as depicted was deduced from the ¹H n.m.r. spectrum by these authors.

X-*Ray Structure Determination of* 4-*Cyanotricyclo*[6.4.0.0^{2,5}]-*dodeca*-1(12),6,8,10-*tetraen*-5-*one* (2).—*Crystal data.* $C_{13}H_9NO$, $M = 195.22$. Monoclinic, $a = 9.351(5)$, $b = 12.242(8)$, $c = 9.217(6)$ Å, $\beta = 105.78(5)°$, $U = 1\,015$ Å^3, $Z = 4$, $D_c = 1.277$ g cm^{-3}, $F(000) = 408$, $\mu(Mo\text{-}K_\alpha) = 0.761$ cm^{-1}. Systematic absences: $h0l$ for l odd, $0k0$ for k odd, space group $P2_1/c$.

A single crystal having dimensions *ca.* $0.5 \times 0.5 \times 0.4$ mm was used for the X-ray experiment. The unit-cell dimensions and the reflection intensities were obtained with a Rigaku automatic four-circle diffractometer at the High Brilliance X-ray Diffraction Laboratory of Hokkaido University, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,73$ Å). The ω–2θ scanning technique was applied at an ω scan rate of 4° min^{-1}; the background was measured for 10 s at each end of the scan range. Three standard reflections, measured at intervals of every 100 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption or the extinction effect. In the range of 2θ values up to 50°, 1 560 independent structure factors above the $\sigma(F)$ level were selected for the structure determination.

The structure was solved by the Monte Carlo direct method,[6] using the 10 strongest reflections as the starting set. An E-map based on the fifteenth random phase set afforded all the non-hydrogen atoms. The structure obtained was refined by the block-diagonal least-squares method with anisotropic temperature factors. After all the hydrogen atoms had been located in a difference-Fourier map, further least-squares refinements were carried out, to include these hydrogen atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\{\sigma(F)^2 \exp(AX^2 + BY^2 + CXY + DX + EY)\}$, where $X = |F_o|$ and $Y = \sin\theta/\lambda$. The A, B, C, D, and E coefficients were evaluated from the $(\Delta F)^2$ distribution; $A = -0.000\,759$, $B = 10.6$, $C = 0.130$, $D = 0.0639$, and $E = -18.7$. The final R value was 5.2%. Atomic co-ordinates for non-hydrogen atoms, bond lengths and angles, and torsion angles are given in Tables 1—3.*

The calculations were carried out on a HITAC M-280H computer at the Hokkaido University Computing Center, using our own programs. The atomic scattering factors were taken from International Tables.[7]

The molecular skeleton of compound (2) is shown in the Figure. The seven-membered ring has a flattened boat
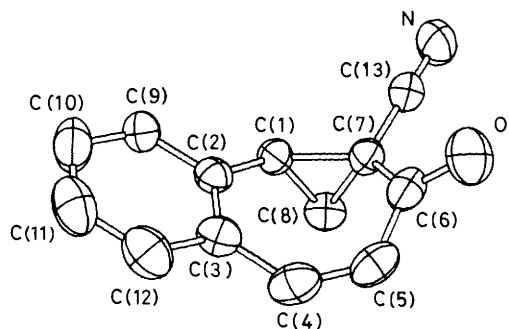

Figure. Perspective view of molecule (2) showing crystallographic numbering scheme

conformation with an approximate mirror plane through the carbonyl group. As Table 3 shows, the cyclopropane ring is approximately bisected by each of the benzene-ring and

* Details of the anisotropic thermal parameters for the non-hydrogen atoms and the co-ordinates and temperature factors for the hydrogen atoms are available in Supplementary Publication No. SUP 56128 (2 pp.). See Instructions for Authors (1985) in *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1. Structure factors are available from the editorial office on request.

Table 1. Fractional atomic co-ordinates (standard deviations in parentheses). Crystallographic numbering scheme is used

Atom	x	y	z
O	0.468 4(3)	0.170 6(2)	0.303 5(2)
N	0.639 3(2)	0.404 7(2)	0.465 4(3)
C(1)	0.283 1(2)	0.438 7(1)	0.212 6(2)
C(2)	0.124 3(2)	0.408 9(2)	0.180 4(2)
C(3)	0.056 3(2)	0.319 0(2)	0.093 5(2)
C(4)	0.133 6(3)	0.232 8(2)	0.036 0(3)
C(5)	0.271 9(3)	0.196 2(2)	0.087 9(3)
C(6)	0.388 4(2)	0.235 0(2)	0.218 9(2)
C(7)	0.413 6(2)	0.354 1(2)	0.244 1(2)
C(8)	0.377 6(2)	0.430 7(2)	0.108 1(2)
C(9)	0.036 3(2)	0.479 0(2)	0.238 3(2)
C(10)	−0.115 2(3)	0.461 1(2)	0.212 5(3)
C(11)	−0.181 6(3)	0.375 4(3)	0.124 9(3)
C(12)	−0.097 8(3)	0.306 4(2)	0.065 4(3)
C(13)	0.539 6(2)	0.381 3(2)	0.368 1(2)

Table 2. Bond lengths (Å) and angles (°) (standard deviations refer to the last digits)

C(1)–C(2)	1.479(3)	C(2)–C(1)–C(7)	124.3(2)
C(1)–C(7)	1.566(3)	C(2)–C(1)–C(8)	126.8(2)
C(1)–C(8)	1.478(3)	C(7)–C(1)–C(8)	60.2(1)
C(2)–C(3)	1.407(3)	C(1)–C(2)–C(3)	125.5(2)
C(2)–C(9)	1.391(3)	C(1)–C(2)–C(9)	115.9(2)
C(3)–C(4)	1.457(3)	C(3)–C(2)–C(9)	118.6(2)
C(3)–C(12)	1.402(3)	C(2)–C(3)–C(4)	125.6(2)
C(4)–C(5)	1.329(3)	C(2)–C(3)–C(12)	118.3(2)
C(5)–C(6)	1.467(3)	C(4)–C(3)–C(12)	116.1(2)
C(6)–C(7)	1.485(3)	C(3)–C(4)–C(5)	130.1(2)
C(6)–O	1.213(3)	C(4)–C(5)–C(6)	128.2(2)
C(7)–C(8)	1.529(3)	C(5)–C(6)–C(7)	119.8(2)
C(7)–C(13)	1.440(3)	C(5)–C(6)–O	120.6(2)
C(9)–C(10)	1.389(4)	C(7)–C(6)–O	119.5(2)
C(10)–C(11)	1.366(4)	C(1)–C(7)–C(6)	122.5(2)
C(11)–C(12)	1.364(4)	C(1)–C(7)–C(8)	57.0(1)
C(13)–N	1.141(3)	C(1)–C(7)–C(13)	115.0(2)
		C(6)–C(7)–C(8)	118.9(2)
		C(6)–C(7)–C(13)	114.4(2)
		C(8)–C(7)–C(13)	117.3(2)
		C(1)–C(8)–C(7)	62.8(1)
		C(2)–C(9)–C(10)	121.3(2)
		C(9)–C(10)–C(11)	120.1(3)
		C(10)–C(11)–C(12)	119.6(2)
		C(3)–C(12)–C(11)	122.2(2)
		C(7)–C(13)–N	178.8(3)

Table 3. Torsion angles (°) (standard deviations refer to the last digits)

C(7)–C(1)–C(2)–C(3)	−38.0(3)
C(8)–C(1)–C(2)–C(3)	38.1(3)
C(1)–C(2)–C(3)–C(4)	7.9(3)
C(2)–C(3)–C(4)–C(5)	26.0(4)
C(3)–C(4)–C(5)–C(6)	−1.3(5)
C(4)–C(5)–C(6)–C(7)	−44.7(4)
C(4)–C(5)–C(6)–O	138.3(3)
C(5)–C(6)–C(7)–C(1)	38.6(3)
C(5)–C(6)–C(7)–C(8)	−28.8(3)
O–C(6)–C(7)–C(13)	2.6(3)
C(2)–C(1)–C(7)–C(6)	10.8(3)

carbonyl planes, while the C(4)=C(5) double bond deviates considerably from both these planes. As a result of this ring conformation, the α hydrogen atom at C(8) approaches the C(5) atom closely, their separation being 2.67(3) Å.

This rearrangement constitutes a two-step preparation of 'benzohomotropone' (2) which is potentially useful for further

transformations, from starting materials abundantly available. The synthesis of tricyclo[6.4.0.0^{2,4}]dodeca-1(12),6,8,10-tetraen-5-one itself has already been reported by two other groups of investigators.[8]

The formation of 'benzohomotropone' (2) involves a new rearrangement. It is the first example of a reorganization of a 6/4 fused ring system to a 7/3 fused ring system. The formation of compound (2) clearly starts from an 8-membered carbon-centred radical (C) which is generated by β-scission of an alkoxyl radical (B) (Scheme).

Probable pathways from the radical (C) that give 'benzo-homotropone' (2) are outlined in the Scheme. Of the ionic and radical pathways depicted in the Scheme the former is perhaps more plausible.

Experimental

M.p.s were recorded with a Yanagimoto micro m.p. apparatus. I.r. spectra were determined for Nujol mulls with a Hitachi Model 285 infrared spectrophotometer. ^{1}H N.m.r. spectra were determined with a JEOL PS 100 high-resolution FT-NMR spectrometer (100 MHz) (solvent CDCl$_3$: SiMe$_4$ as internal standard) (Faculty of Pharmaceutical Sciences of this University). T.l.c. was carried out on Merck Kiesel gel 60 PF$_{254}$. The low-resolution mass spectrum was determined with a JEOL JMS-D-300 spectrometer (70 eV).

endo-4-*Cyanotricyclo*[6.4.2.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraen-5-ol* (1).—This cyclobutanol was prepared according to the procedure reported. M.p. 93—94 °C (lit.,[4] 94—95 °C).

Irradiation of Hypoiodite of endo-4-*Cyanotricyclo*[6.4.0.0^{2,5}]*dodeca*-1(12),6,8,10-*tetraen-5-ol*.—The cyclobutanol (1) (500 mg, 2.5 mmol), dissolved in benzene (60 ml) containing mercury(II) oxide (600 mg, 2.75 mmol) and iodine (700 mg, 2.75 mmol) in a Pyrex vessel, was irradiated with a 100-W high-pressure Hg arc for 5 h under nitrogen. The solution was filtered and the filtrate was washed twice with 5% aqueous sodium thiosulphate and then with water. The solution was dried over anhydrous sodium sulphate. After evaporation of the solvent, the residue was subjected to preparative t.l.c. with 10:1 benzene–diethyl ether as developer to give benzohomotropone (2) (40%). Recrystallization from diethyl ether–light petroleum (b.p. 30—60 °C) gave crystals of benzohomotropone (2) (100 mg, 20%), m.p. 130—132 °C (Found: C, 79.7; H, 4.7; N, 7.3. C$_{13}$H$_9$NO requires C, 79.98; H, 4.65; N, 7.1%); $\nu_{max.}$ 2 245 (C≡N) and 1 650 cm^{-1} (C=O); δ_H 7.28—7.56 (4 H, m, ArH), 6.94 (1 H, d, *J* 13.18 Hz, 7-H), 6.06 (1 H, d, *J* 13.18 Hz, 6-H), 3.28 (1 H, dd, *J* 9.28 and 9.76 Hz 2-H), 2.47 (1 H, dd, *J* 9.76 and 5.62, 3-H), 2.35 (1 H, dd, *J* 9.28 and 5.62 Hz, 3-H), δ_C 189.6 (s, C-5), 139.7 (d, C-7), 135.4 (s, C-8), 133.9 and 131.9 (d) (C-9, -10, -11, and -12), 130.6 (d), 128.3 (d), 131.1 (s, C-1), 124.5 (d, C-6), 118.0 (s, CN), 37.9 (d, C-2), 26.9 (s, C-4), and 22.1 (t, C-3); $\lambda_{max.}$(EtOH), 292 (ε 4 900 dm^3 mol^{-1} cm^{-1}), 223sh, and 209 nm (10 100).

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