and 2.52–2.60 (m, 2, H_9), 3.44–3.50 (m, 3, H_{10}), 5.27–5.29 (dd, 1, $J_{8,9}$ = 2.2, $J_{8,9'}$ = 5.9 Hz, H_8), 7.93–8.20 (m, 7, $H_{1-5,11,12}$), 8.51(s, 1, H_6).

cis-7,8-Diacetoxy-7,8-dihydro-1 (7). Reaction of 6 with DDQ under the same conditions (except at 55 °C) as described for 5 gave 7 in 93% yield: mp 252–253 °C; mass spectrum, *m/e* 384 (M^+); NMR (CDCl$_3$) δ 1.65 (s, 3, CH$_3$), 1.98 (s, 3, OAc), 2.06 (s, 3, OAc), 5.22 (d, 1 H$_8$), 6.52 (dd, 1, H$_{10}$), 7.72 (d, 1, H$_{10}$), 8.00–8.21 (m, 6, aromatic), 8.38 (d, 1, H$_{11}$), 8.56 (s, 1, H$_6$) ($J_{8,9}$ = 5.2, $J_{9,10}$ = 10.3, $J_{10,11}$ = 9.56 Hz).

cis-7,8-Dihydroxy-7,8-dihydro-1 (2a). Methanolysis of 7 with NaOCH$_3$ under conditions as described for 2b gave 2a in 78% yield: mp 240–242 °C; mass spectrum, *m/e* 300 (M^+); NMR (acetone-d_6) δ 1.52 (s, 3, CH$_3$), 4.08 (d, 1, H$_8$), 6.52 (dd, 1, H$_9$), 7.72 (d, 1, H$_{10}$), 8.00–8.61 (m, 8, aromatic) ($J_{8,9}$ = 5.9, $J_{9,10}$ = 9.6, $J_{8,10}$ < 0.5 Hz).

Synthesis of Acetonide of 2a. This compound was synthesized according to the published procedure[8] in 95% yield; mass spectrum, *m/e* 249, 254, 282, 283, 340 (M^+). The UV absorption characteristics are closely similar to those of 2a.

Acknowledgment. We thank Dr. D. W. Miller for obtaining the ^{1}H NMR spectra, and Mr. J. Clark and Mrs. A. Y. Haung for technical assistance.

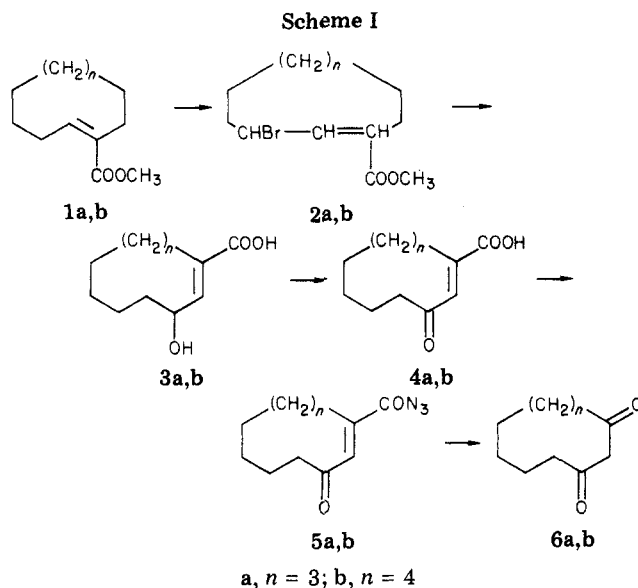# A New Synthesis of Cyclodecane- and Cycloundecane-1,3-dione

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Continuing our work on the photochemical behavior of the isoxazolophanes,[1] we found it necessary to find an entry to cyclodecane- and cycloundecane-1,3-dione. The method should be simpler than the one reported in the literature[2] which used cyclododecanone and cycloundecanone, respectively, as the starting materials. We now report a new synthesis (Scheme I) of the title compounds starting from (methoxycarbonyl)cyclodec-1-ene (1a) and its homologue 1b.[3] Allylic bromination with NBS of the starting materials afforded in both cases only the 3-bromo derivatives (2a,b). Although the reaction is stereospecific, we have not elements to assign univocally the stereochemistry of 2a,b.

From 2a,b the corresponding hydroxy acids (3a,b) were obtained by reaction with KOH–H$_2$O–Me$_2$SO, in 48–50% yield, purifiable as the insoluble K salt. Jones oxidation of 3a,b, gave the 3-oxo acids (4a,b) which were converted into the acyl azides (5a,b) via the mixed anhydride method.[4] Thermal decomposition of the acyl azides 5a,b followed by acidic treatment of the intermediate isocyanate afforded the 1,3-diones (6a,b).

Scheme I

a, *n* = 3; b, *n* = 4

The advantages of this synthesis are (i) availability of our starting materials which served only as intermediates for the preparation of starting materials (cyclodecanone and cycloundecanone) in the reported synthesis,[2] (ii) a fewer number of chemical steps with good overall yields, via stable and purifiable intermediates.

The stereochemistry of the double bonds, as reported in Scheme I, was assigned on the basis of the following data: (i) the methyl esters of 3b and 4b were identical with known compounds;[5] (ii) the chemical shifts of the vinyl protons of compounds 3a–5a are in agreement with those of cycloundecene derivatives 3b–5b; (iii) the chemical shift of the vinyl proton of the methyl ester of 4a is at δ 7.29; short-time irradiation of this methyl ester allows to show the presence of its isomerization product which is intermediate in the photochemical deconjugation reaction leading to a mixture of the known[6] (*E*)- and (*Z*)-3-(methoxycarbonyl)cyclodec-3-enones; the chemical shift of vinyl proton of the above unisolable intermediate ester is at higher field (δ 6.46), inferred from the reaction mixture, than that of the methyl ester of 4a, supporting the *E* configuration of the latter in agreement with a literature report.[7] NaBH$_4$ reduction of the methyl ester of 4a affords the same hydroxy ester obtained from 3a with CH$_2$N$_2$.

Experimental Section

Melting points were taken on a Büchi apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Varian EM-390 instrument; chemical shifts are reported in parts per million from internal Me$_4$Si. Infrared spectra were recorded on a Perkin-Elmer 377 spectrophotomer. UV spectra were taken on a Varian Cary 219 (EtOH solutions).

1-(Methoxycarbonyl)-3-bromocycloalk-1-ene (2a,b). A mixture of (methoxycarbonyl)cycloalk-1-ene (1a,b; 0.2 mol), azobis(isobutyronitrile) (0.5 g), and NBS (0.21 mol) in CCl$_4$ (300 mL) was heated under reflux, with stirring, for 2 h. [Caution: The reaction may start very exothermically.] After cooling, the reaction mixture was filtered, and the filtrate was washed with water (2 × 50 mL) and dried. The residue from the solvent evaporation afforded the bromo ester (2a,b). 2a: 46 g, 83.6%, as undistillable oil; NMR (CDCl$_3$) 6.9 (1 H, d, *J* = 11 Hz), 5.3 (1 H, m), 3.8 (3 H, s), 2.55 (2 H, m), 2.3 (2 H, m), 1.4 (10 H, m); IR (film) 1710, 1630 cm^{-1}. 2b: 29.6 g; 51.3%; mp 64 °C.[5]

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3-Hydroxycycloalk-1-enecarboxylic Acid (3a,b). The bromo ester (2a,b; 0.2 mol) was dissolved in Me_2SO (200 mL) and then a solution of KOH (20 g) in water (35 mL) was added at room temperature. After being stirred for 1 h, the mixture was cooled to 5 °C and filtered. The filtered K salt was suspended in water (100 mL) and dilute H_2SO_4 added (20%, 100 mL). Filtration afforded the hydroxy acids (3a,b). **3a:** 19.1 g; 48.2%; mp 152 °C from acetone–Et_2O; NMR (Me_2SO) 12.2 (1 H, s), 6.48 (1 H, d, J = 10 Hz), 4.8 (1 H, s), 4.6 (1 H, m), 2.5 (2 H, m), 1.4 (12 H, m); IR (Nujol) 3450, 1700, 1650 cm^{-1}; UV 215 nm (ϵ 10 500). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.46; H, 9.23.

3b: 21.5 g; 50.7%; mp 149 °C from acetone–Et_2O; NMR (Me_2SO) 6.43 (1 H, d, J = 10 Hz), 4.48 (2 H, m, CHOH and CHOH), 2.5 (4 H, m), 1.4 (12 H, m); IR (Nujol) 3400, 1710, 1680, 1650 cm^{-1}; UV 216 nm (ϵ 9100). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.44; H, 9.61.

3-Oxocycloalk-1-enecarboxylic Acid (4a,b). The hydroxy acid (3a,b; 0.1 mol) was dissolved in acetone (200 mL) and oxidized with an excess of Jones reagent at 10 °C. Usual workup afforded the corresponding keto acid (4a,b). **4a:** 17.4 g; 89%; mp 144 °C from Et_2O–pentane; NMR ($CDCl_3$) 11.2 (1 H, s), 7.32 (1 H, s), 2.6 (4 H, m), 1.9–1.2 (10 H, m); IR (Nujol) 1700, 1635 cm^{-1}; UV 232 nm (ϵ 5800). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.44; H, 8.18.

4b: 19.9 g; 95%; mp 94 °C from Et_2O–pentane; NMR ($CDCl_3$) 10.7 (1 H, s), 7.33 (1 H, s), 2.8 (2 H, m), 2.55 (2 H, m), 1.9–1.2 (12 H, m); IR (Nujol) 1695, 1630 cm^{-1}; UV 239 nm (ϵ 7300). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.36; H, 8.54.

3-Oxocycloalk-1-enecarbonyl Azide (5a,b). To a solution of the keto acid (4a,b; 0.1 mol) in acetone (150 mL) and water (50 mL) at 0 °C was added triethylamine (0.12 mol) followed by the slow addition of ethyl chloroformate (0.11 mol) in acetone (25 mL). The mixture was stirred for 30 min at 0 °C and then a solution of sodium azide (0.15 mol) in water (30 mL) was added dropwise. After 30 min of stirring, the mixture was poured into water (300 mL) and extracted with Et_2O (2 × 150 mL). The ether extract was washed with water and dried. Solvent was removed in vacuo at room temperature to leave the 3-oxocycloalk-1-enecarbonyl azide (5a,b). **5a:** 17.9 g; 81%; mp 73–75 °C from pentane; NMR ($CDCl_3$) 7.34 (1 H, s), 2.6 (4 H, m), 1.9 (2 H, m), 1.6–1.2 (8 H, m); IR (Nujol) 2160, 1700, 1640 cm^{-1}; UV 237 nm (ϵ 11 600). Anal. Calcd for $C_{11}H_{15}O_2N_3$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.59; H, 6.90; N, 18.81.

5b: 21.6 g; 92%; mp 55.5–56.5 °C from pentane; NMR ($CDCl_3$) 7.27 (1 H, s), 2.77 (2 H, m), 2.5 (2 H, m), 1.9–1.2 (12 H, m); IR (Nujol) 2150, 1700, 1630 cm^{-1}; UV 247 nm (ϵ 9400). Anal. Calcd for $C_{12}H_{17}O_2N_3$: C, 61.25; H, 7.28; N, 17.86. Found: C, 61.16; H, 7.32; N, 17.78.

Cycloalkane-1,3-dione (6a,b). The 3-oxocycloalk-1-ene-carbonyl azide (5a,b; 0.1 mol) was dissolved in dry benzene (300 mL) and the solution was then heated until no more nitrogen evolved (1 h). Removal of benzene in vacuo afforded a liquid which was dissolved in dioxane (90 mL); 15% aqueous hydrochloric acid (300 mL) was then added and the mixture heated under reflux for 1.5 h. After cooling, the mixture was extracted with Et_2O (3 × 100 mL). The Et_2O extract was washed with water and dried. Vacuum distillation of the residue from the solvent evaporation afforded pure cycloalkane-1,3-dione (6a,b). **6a:** 11.1 g; 66%. **6b:** 12.2 g; 67%.

Methyl Ester of 4a. This compound was obtained in quantitative yield by esterification of 4a with CH_2N_2: mp 69.5–70.5 °C from hexane; NMR ($CDCl_3$) 7.29 (1 H, s), 3.78 (3 H, s), 2.55 (4 H, m), 2–1.1 (10 H, m); IR (Nujol) 1705, 1685, 1610 cm^{-1}; UV 230 nm (ϵ 7600). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.67.

Irradiation of the Methyl Ester of 4a. The methyl ester of 4a (1 g) was dissolved in benzene (300 mL), N_2 was bubbled through the solution for 5 min, and irradiation (high-pressure Hg lamp, 125 W, Pyrex filter) was carried out for 8 h. After solvent evaporation, silica gel (30 g) column chromatography of the residue (eluant hexane–Et_2O, 9:1 v/v) afforded (Z)- (353 mg) and (E)-3-(methoxycarbonyl)cyclodec-3-enone (560 mg).

The NMR ($CDCl_3$) spectrum of the photolysate mixture at short-time irradiation (1.5 h) shows the presence of four unsaturated products: the starting Δ^2 isomer (17%, s, δ 7.29), the (E)-Δ^3 isomer (54%, t, δ 6.98), the (Z)-Δ^3 isomer (12%, t, δ 6.17), and the stereoisomer of the starting material (17%, s, δ 6.46).

Communications

Relative Stabilities of Secondary Methylnorbornyl Cations

Summary: Force-field calculations are used to examine alternative comparisons for the energetics of rearranging secondary carbocations in the alicyclic and norbornyl series to their tertiary isomers.

Sir: The heat of isomerization of the secondary 4-methyl-2-norbornyl cation (1) to the tertiary 2-methyl-2-norbornyl cation (2) (eq 1) has been recently reported.[1] Comparison with the isomerization of the secondary butyl to the tertiary butyl cation (eq 2) led to the conclusion that 2 enjoys special thermodynamic stability amounting to ca. 7.6 kcal/mol, but the source of this difference could not be established by this single experiment.[1,2] Since no other stable secondary ions could be found whose heat of isomerization in solution might reasonably be determined ex-

$$\text{1} \longrightarrow \text{2} \qquad ; \Delta H_1 = -6.6 \text{ Kcal/mol} \qquad (1)$$

$$\longrightarrow \qquad ; \Delta H_2 = -14.2 \text{ Kcal/mol} \qquad (2)$$
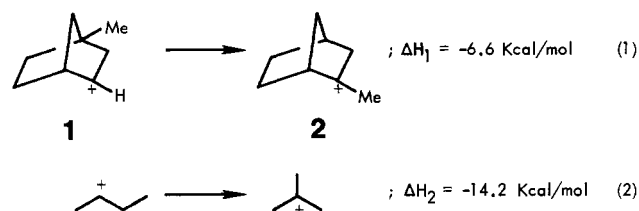
perimentally,[2] it appeared that our base of comparison could be expanded through molecular mechanics (force field) calculations. This method has been applied fruitfully for the calculation of carbocation stabilities and those of related transition states.[3] Until other experimental ex-

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