Conversion of Bicyclic αα-Dichlorocyclobutanones into Monocyclic β-Formyl Esters and Bicyclic Cyclopropanes with Silver Tetrafluoroborate

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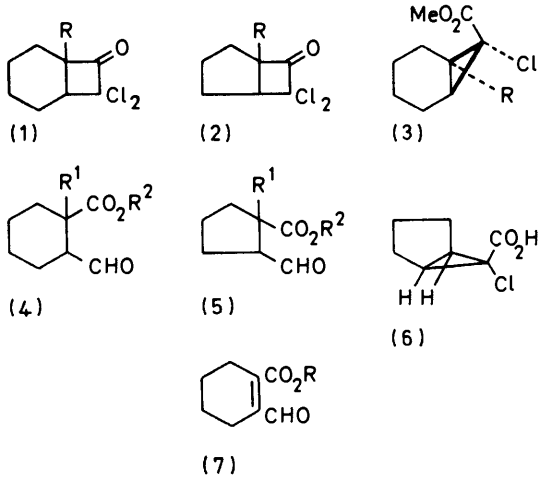
Bicyclic αα-dichlorocyclobutanes (1) and (2) (R = H), treated with silver tetrafluoroborate in aqueous alcoholic solution, gave bicyclic α-chlorocyclopropanecarboxylic acids and esters (3) and (6) together with monocyclic β-formyl esters (4), (5), and (7) (R = H). The alkoxy-derivatives of (1) and (2) (R = alkoxy), however, gave only the β-formyl esters (4), (5), and (7) (R = alkoxy).

REACTIONS of bicyclic αα-dichlorocyclobutanones [1] obtained by cycloaddition of dichloroketen [1-3] to cyclic olefins, and of αα-dichlorobicyclo[3.2.0]heptanols [4] with various bases [2,5] have been reported.

In the present work the adducts of cyclohexene, cyclopentene, and their alkoxy-derivatives were treated

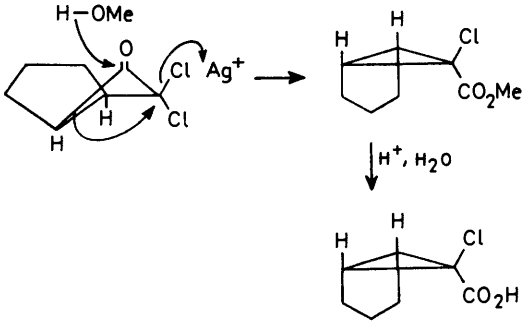


with silver tetrafluoroborate in boiling aqueous methanol or ethanol to give various products, mainly a mixture of isomeric β-formyl esters (4) and (5) which we were unable to separate by column chromatography or t.l.c.

In two cases, with the adducts [(1) and (2) (R = H)] of the unsubstituted olefins, ring-contraction products were isolated, *viz.* α-chlorocyclopropanecarboxylic acids and esters. Thus 8,8-dichlorobicyclo[4.2.0]octan-7-one (1; R = H) afforded methyl *exo*-7-chlorobicyclo[4.1.0]-heptane-*endo*-7-carboxylate (3; R = H) and methyl *trans*-2-formylcyclohexanecarboxylate (4; R^1 = H, R^2 = Me) in roughly equal amounts in methanolic solution. The chloro-substituent in the ester (3; R = H) was assigned the *exo*-configuration since it was resistant to catalytic hydrogenolysis at atmospheric pressure (10% Pd–C) (*cf.* the hydrogenolysis of dibromo- to monobromo-cyclopropanes [6,7]).

7,7-Dichlorobicyclo[3.2.0]heptan-6-one (2; R = H) gave *exo*-6-chlorobicyclo[3.1.0]hexane-*endo*-6-carboxylic acid (6) and its methyl ester, but no simple cyclopentane derivatives were isolated. Conversely, none of the alkoxycyclobutanones (1) and (2) (R = OMe or OEt) gave bicyclic ring-contraction products; only β-formyl esters of types (4), (5), and (7) were obtained.

Ring fission of cyclobutanes to give alicyclic compounds and ring contraction to give cyclopropane derivatives have been shown to involve bicyclobutylium ions.[8] There is less probability however, in the present conversions, of prior loss of chloride ion to give a carbocation, as this would be opposed by the inductive effect of the second chlorine atom; instead a concerted ' push–pull ' mechanism (Scheme 1) is possible.



SCHEME 1

Relief of ring strain could be effected similarly by fission of the Cl_2C–CO bond through acid catalysis, assisted by the inductive effects of both chlorine atoms (Scheme 2). The conversion of the dichloromethyl intermediate (8) into the aldehyde could then proceed through the *gem*-diol.

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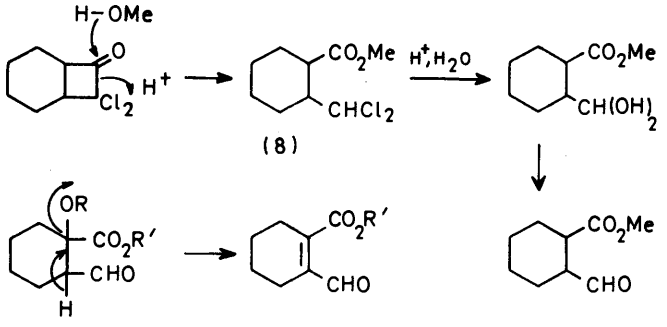
The failure of alkoxy-substituted cyclobutanones (1) and (2) (R = OMe or OEt) to undergo ring contraction may be due to steric effects imposed by the bulky



SCHEME 2

alkoxy-groups, which would prevent further increase of strain at C(6),C(7) in (2) or C(7),C(8) in (1). In any event, the α-chlorocyclopropanecarboxylic acids or esters (3; R = OMe or OEt) would be unstable under the reaction conditions: dihalogenocarbene adducts of simple enol ethers have been shown to undergo ready fission of the cyclopropane ring under similar conditions.[9] The αβ-unsaturated β-formyl esters (7) could presumably arise by loss of ROH from the products (4) and (5) (Scheme 2).

EXPERIMENTAL

I.r., u.v., and ^{1}H n.m.r. spectra were recorded with Unicam SP 1000, Unicam SP 800, and Varian A60 or Perkin-Elmer R21 instruments, respectively. Petroleum refers to the fraction of b.p. 60—80 °C. Unless otherwise stated the solvent system used for chromatography was a mixture of ethyl acetate (A) and petroleum (B). Mild oxidation of β-formyl esters was performed with silver oxide–sodium hydroxide at room temperature.

1-Alkoxycyclo-hexenes and -pentenes.—These were prepared according to modified versions of published methods.[10] Redistilled cyclo-hexanone or -pentanone (0.6 mol) and triethyl orthoformate (0.66 mol) were mixed; naphthalene-2-sulphonic acid (0.4 g) was added and the mixture was heated at 100 °C until no more ethyl formate distilled over. The temperature was then raised to 180—190° for *ca.* 2 h, during which ethanol distilled off. Careful fractionation of the residue *in vacuo* gave the enol ether in 70—85% yield. Similarly, 1-methoxycyclo-hexene and -pentene were obtained by using trimethyl orthoformate.

8,8-Dichlorobicyclo[4.2.0]octan-7-one (1; R = H).—A mixture of triethylamine (9.60 g, 0.095 mol) and sodium-dried n-pentane (20 ml) was added dropwise over 30 min to a stirred ice-cooled solution of cyclohexene (21.48 g, 0.262 mol) and dichloroacetyl chloride (12.98 g, 0.088 mol) in n-pentane (100 ml). The mixture was then stirred for 30 min more and the triethylamine hydrochloride formed was filtered off. The n-pentane solution was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* giving a yellow *oil* (14.1 g), which was distilled. The other dichlorocyclobutanones (see Table) were obtained similarly.

Reactions with Silver Tetrafluoroborate in Aqueous Methanol.—(a) *8,8-Dichlorobicyclo[4.2.0]octan-7-one* (1; R = H). The ketone (1; R = H) (5.29 g, 0.027 mol) in methanol (70 ml) was boiled under reflux for 10 h with aqueous tetrafluoroborate solution [from silver oxide (6.9 g, 1.1 mol) and tetrafluoroboric acid (42%; 11.2 g)]. Sodium chloride (5.3 g) in water (15 ml) was then added and the precipitated silver salts were filtered off and washed with small amounts of hot methanol. The filtrate and washings were concentrated to *ca.* 20 ml and extracted with ether (× 3; *ca.* 120 ml total). The extracts were dried and evaporated *in vacuo* to a brown residue (3.6 g). Column chromatography (alumina grade II; A–B, 1 : 20) gave (i) *methyl* exo-*7-chlorobicyclo[4.1.0]heptane*-endo-*7-carboxylate*, a liquid (1.8 g, 34.8%) (Found: C, 57.4; H, 6.9; Cl, 19.1. $C_9H_{13}ClO_2$ requires C, 57.3; H, 6.9; Cl, 18.8%), R_F 0.62 (alumina II; A–B, 1 : 15), $\nu_{max.}$ (film) 1 720, 1 160, and 1 120 cm^{-1}, τ ($CDCl_3$) 6.40 (3 H, s, OMe) and 8.10—8.88 (10 H, m); and (ii) methyl *trans*-2-formylcyclohexane-1-carboxylate, a liquid (34.4%), b.p. 70° at 33 mmHg, R_F

Dichlorocyclobutanones (1) and (2)

	R	Yield (%)	B.p. (°C) [mmHg]	Formula	Analysis (%) [a] C	H	Cl	n_D^{25}	$\nu_{max.}$(cm^{-1} (film)
(1)	H	66	95 [2] [b]	$C_8H_{10}Cl_2O$	49.6 (49.7)	5.1 (5.2)	36.75 (36.8)	1.507 3	1 800vs
(1)	OMe	60	88 [0.05]	$C_9H_{12}Cl_2O_2$	48.35 (48.4)	5.25 (5.4)	31.6 (31.8)		1 790vs, 1 100, 1 080, 1 040
(1)	OEt	62.6	90—92 [0.05]	$C_{10}H_{14}Cl_2O_2$	50.4 (50.6)	5.8 (5.9)	29.95 (30)	1.491 0	1 790vs, 1 110, 1 080, 1 035
(2)	H	55.9	46 [0.2] [c]	$C_7H_8Cl_2O$	46.75 (46.9)	4.5 (4.5)	39.6 (39.7)	1.499 5	1 790vs
(2)	OMe	33	78 [1.5]	$C_8H_{10}Cl_2O_2$	45.8 (45.9)	4.7 (4.8)	33.9 (34)		1 785vs, 1 110, 1 080, 1 037
(2)	OEt	35	76 [2]	$C_9H_{12}Cl_2O_2$	48.25 (48.4)	5.3 (5.4)	31.7 (31.8)	1.525 0	1 800vs, 1 100, 1 080, 1 040

[a] Required values in parentheses. [b] Lit.,[1] b.p. 93—94° at 2.5 mmHg; $\nu_{max.}$ 1 800 cm^{-1}(CO). [c] Lit.,[2] b.p. 73° at 1.5 mmHg: n_D^{25} 1.499 9.

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0.15, $\nu_{max.}$ (film) 1 740, 1 080, and 960 cm^{-1}; 2,4-dinitrophenylhydrazone, orange needles (from methanol), m.p. 138—139°; $\lambda_{max.}$ ($CHCl_3$) 368 nm (ε 21 200). Oxidation of the latter gave methyl hydrogen cyclohexane-*trans*-1,2-dicarboxylate, identical with an authentic specimen [11,12] (m.p. and mixed m.p. 54°).

(b) 8,8-*Dichloro*-6-*methoxybicyclo*[4.2.0]*octan*-7-*one* (1; R = OMe). Column chromatography (silica; A–B, 1 : 1) of the product obtained as above from (1; R = OMe) gave (i) *methyl* 2-*formyl*-1-*methoxycyclohexanecarboxylate* (4; R^1 = OMe, R^2 = Me), a liquid (18.3%), b.p. 75° at 0.05 mmHg; R_F 0.44 (alumina II; A–B, 1 : 5) (Found: C, 60.15; H, 8.0. $C_{10}H_{16}O_4$ requires C, 60.0; H, 8.0%), $\nu_{max.}$ (film) 1 720, 1 620, 1 200, 1 140, and 1 120 cm^{-1}, τ ($CDCl_3$) 0.58 (1 H, t, *J* 5 Hz, CHO), 6.08 (3 H, s, CO_2Me), 6.63 (3 H, s, OMe), and 7.03—9.13 (9 H, m); and (ii) *methyl* 2-*formylcyclohex*-1-*enecarboxylate* (7; R = Me), a liquid (5%), b.p. 82° at 0.05 mmHg, R_F 0.25 (Found: C, 64.25; H, 7.0. $C_9H_{12}O_3$ requires C, 64.3; H, 7.1%), $\nu_{max.}$ (film) 1 720, 1 680, 1 615, 1 160, and 1 135 cm^{-1}, τ ($CDCl_3$) 0.55 (1 H, t, *J* 5 Hz, CHO), 6.35 (3 H, s, OMe), and 7.45—8.15 (8 H, m). Oxidation of the latter gave cyclohex-1-ene-1,2-dicarboxylic acid, m.p. 126° (lit.,[13] 126°).

(c) 7,7-*Dichlorobicyclo*[3.2.0]*heptan*-6-*one* (2; R = H). The product mixture, a brown semi-solid (2.0 g, from 5.37 g of ketone), was washed with cold petroleum (*ca.* 20 ml) to afford (i) *exo*-6-chlorobicyclo[3.1.0]hexane-*endo*-6-carboxylic acid (6), rhombic crystals (24%) (from petroleum), m.p. 118—121° (Found: C, 52.4; H, 5.7; Cl, 21.8. Calc. for $C_7H_9ClO_3$: C, 52.35; H, 5.6; Cl, 22.0%), $\nu_{max.}$ (Nujol) 3 000, 2 820, 2 700, and 1 720 cm^{-1}, identical with an authentic specimen [4] (mixed m.p. 118—120°); and (ii) *methyl* exo-6-*chlorobicyclo*[3.1.0]*hexane*-endo-6-*carboxylate* (from evaporation of the petroleum filtrate), a liquid (11.5%), b.p. 58° at 0.4 mmHg (Found: C, 55.0; H, 6.25; Cl, 20.2. $C_8H_{11}ClO_2$ requires C, 55.0; H, 6.3; Cl, 20.3%), n_D^{25} 1.475 0, $\nu_{max.}$ (film) 2 960 and 1 745 cm^{-1}. The latter product and a sample prepared by esterification of the acid had identical refractive indices, i.r. spectra, and b.p.s.

(d) 7,7-*Dichloro*-5-*methoxybicyclo*[3.2.0]*heptan*-6-*one* (2; R = OMe). The products were (i) *methyl* 2-*formyl*-1-*methoxycyclopentanecarboxylate* (5; R^1 = OMe, R^2 = Me), a liquid (30%), b.p. 66—67° at 0.5 mmHg, n_D^{25} 1.488 0 (Found: C, 58.0; H, 7.5. $C_9H_{14}O_4$ requires C, 58.1; H, 7.5%), $\nu_{max.}$ (film) 1 720, 1 100, and 1 080 cm^{-1}, τ ($CDCl_5$) 0.5 (1 H, d, CHO), 6.55 (3 H, s, CO_2Me), 6.23 (3 H, s, OMe), and 7.10—8.70 (7 H, m); and (ii) *methyl* 2-*formylcyclopent*-1-*enecarboxylate*, a liquid (12%), b.p. 80° at 1.5 mmHg (Found: C, 62.2; H, 6.3. $C_8H_{10}O_3$ requires C, 62.3; H, 6.5%,), $\nu_{max.}$ (film) 1 680, 1 640, 1 600, and 1 115 cm^{-1}, τ ($CDCl_3$) 0.47br (1 H, s, CHO), 6.50 (3 H, s, CO_2Me), and 7—8.5 (6 H, m); 2,4-*dinitrophenylhydrazone*, yellowish needles (from ethyl acetate), m.p. 228—230°; *semicarbazone*, leaflets (from chloroform), m.p. 199—201°. Oxidation of the formyl ester gave cyclopent-1-ene-1,2-dicarboxylic acid, m.p. 178° (from ethyl acetate) (lit.,[14] 178°).

Reaction of 7,7-*Dichloro*-5-*ethoxybicyclo*[3.2.0]*heptan*-6-*one* (2; R = OEt) *with Silver Tetrafluoroborate in Ethanol*.—The main product was *ethyl* 2-*formylcyclopent*-1-*enecarboxylate*, obtained through column chromatography (alumina II; A–B 1 : 5) (50%); b.p. 52—56° at 0.2 mmHg (Found: C, 61.4; H, 7.5. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%), $\nu_{max.}$ (film) 1 685, 1 640, 1 600, and 1 100 cm^{-1}; τ ($CDCl_3$) 0.45br (1 H, s, CHO), 6.55 (2 H, q, *J* 7 Hz, O·CH_2·CH_3), 8.12 (3 H, t, *J* 7 Hz, O·CH_2·CH_3), and 7—8.9 (6 H, m). Oxidation gave cyclopentene-1,2-dicarboxylic acid, identical with that obtained from the methyl ester analogue.

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