Synthesis of α-Alkoxycarbonylcycloalkanones by Electrolysis of 1-Trimethylsiloxybicyclo[*n*.1.0]alkanes

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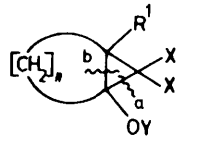
Summary The α-alkoxycarbonylcycloalkanones (**4**) were synthesized in 39—79% yields from the (*n*+3),(*n*+3)-dichloro-1-trimethylsiloxybicyclo[*n*.1.0]alkanes (**1c**; *n*= **4**, 5, and 10) by electrolysis in alcohols in the presence of iron (III) nitrate at −13 to −10 °C.

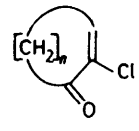
1-TRIMETHYLSILOXYBICYCLO[*n*.1.0]ALKANES (**1a**, **1b**, and **1c**) undergo ring cleavage reactions at bond a or b of the cyclopropane ring. The regioselectivity of the bond fission of (**1a**) seems to be dependent on conditions; *i.e.*, base-catalysed ring opening occurs at bond a[1] and homolytic

cleavage with iron(III) chloride at bond b.[2] Refluxing of (**1b**) in benzene for 5 h and/or allowing (**1b**) to stand in methanolic hydrochloric acid at room temperature gives ring homologation products (**2**) by fission of bond b.[3] In contrast, Schäfer *et al.* have found that anodic oxidation of (**1f**) affords the acyclic ω-dichlorovinylidene esters (**3**; $n = 4$, 5, and 6), preferentially.[4] As part of our programme on development of electrosynthetic reactions, we have found a convenient method for the introduction of an alkoxycarbonyl group at the α-position of cycloalkanones, which involves a novel anodic cleavage at bond a of (**1c**) in the presence of iron(III) nitrate in alcohols, leading to the formation of the β-keto esters (**4**).[5]

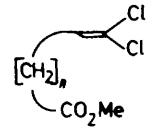


(1)

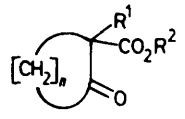
a; $R^1 = H$, $Y = SiMe_3$, $X = H$
b; $R^1 = H$, $Y = SiMe_3$, $X = Br$
c; $R^1 = H$, $Y = SiMe_3$, $X = Cl$
d; $R^1 = Me$, $Y = SiMe_3$, $X = Cl$
e; $R^1 = Y = H$, $X = Cl$
f; $R^1 = H$, $Y = Et$, $X = Cl$



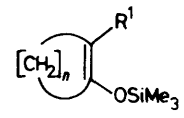
(2)



(3)



(4)



(5)

A typical electrolysis procedure is as follows: a solution of (**1c**; $n = 4$; 0·45 mmol), $LiClO_4.3H_2O$ (6·23 mmol), and $Fe(NO_3)_3.9H_2O$ (0·46 mmol) in MeOH (95 ml) was added to the anode compartment of an electrolysis cell.[6] The cathode compartment contained a solution of $LiClO_4.3H_2O$ (1·24 mmol) in MeOH (23 ml). The mixture was electrolysed with a constant current of 0·003 A/cm,[2] terminal voltage 5 V (cell voltage *ca.* 1·3 V *vs.* SCE), using platinum electrodes (6 cm^2) at −13 to −10 °C for 30 min. The methanolic solution in the anode compartment was concentrated and the residue was taken up in ether–benzene (1:1). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, hexane–ether, 10:1) to give a 72% yield of (**4**; $n = 4$; $R^1 = H$, $R^2 = Me$). Other results are given in the Table. In contrast 1-trimethylsiloxy-6,6-dichlorobicyclo[3.1.0]hexane (**1c**; $n = 3$) afforded exclusively the corresponding ring homologation product (**2**; $n = 3$); other bicyclo[*n*.1.0]alkane systems (**1c**; $n = 4$, 5, and 10) were not obtained. The ester (**3**; $n = 4$) could be obtained in the electrolysis of (**1c**) and/or (**1e**)† under the same conditions as described for (**1c**), except that the iron(III) nitrate was omitted.

An important feature of the reaction is the fact that temperature has a profound effect on the yields of (**4**); the best results were obtained at −13 to −10 °C, yields decreasing above or below this temperature range. Higher temperatures favoured the formation of the ring homologation products (**2**; $n = 4$).

TABLE. Yields of α-alkoxycarbonylcycloalkanones (**4**) from (**1c**)[a] and (**1d**)[a]

$-[CH_2]_n-$	α-Alkoxycarbonylcycloalkanones (**4**)[b]		
n	R^1	R^2[c]	Yield,[d] %
4	H	Me	72
4	H	Et	77
5	H	Me	73
5	H	Et	97
10	H	Me	39[e]
10	H	Et	48[e]
4	Me	Me	56
4	Me	Et	61

[a] The 1-trimethylsiloxy-(*n*+3),(*n*+3)-dichlorobicyclo[*n*.1.0]-alkanes (**1c**) and (**1d**) were prepared as follows: 50% aqueous NaOH (1 ml) was added to a stirred mixture of (**5**; 1 mmol) and benzyltriethylammonium chloride (0·022 mmol) in $CHCl_3$ (10 ml) for 10 min at 3—4 °C. The mixture was worked up and gave (**1c**) and (**1d**) in 87—94% yield. Satisfactory analytical and spectral data were obtained for the new compounds (**1c**; $n = 4$, 5, and 10; **1d**; $n = 4$). [b] Ref. 5. [c] R^2 refers to the alcohol (MeOH or EtOH) used as electrolysis solvent. [d] Based on isolated yields. [e] The low solubility of (**1c**; $n = 10$) in alcohols suppresses the formation of (**4**; $n = 10$).

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† The alcohol (**1e**; $n = 4$) was prepared quantitatively from (**1c**; $n = 4$) by stirring in MeOH for 1·5 h at 0—5 °C: i.r. (neat) 3300 cm^{-1} (OH); δ ($CDCl_3$) 2·72 (s, 1H, OH).

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[3] P. Amice, L. Blanco, and J. M. Conia, *Synthesis*, 1976, 196.
[4] M. Klehr and H. J. Schäfer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 247.
[5] L. Ruest, G. Blourin, and P. Deslongchamps, *Synth. Comm.*, 1976, **6**, 169 and references cited therein.
[6] S. Torii, H. Tanaka, and T. Okamoto, *Bull. Chem. Soc. Japan*, 1972, **45**, 2783.