

## Synthesis of $\alpha$ -Alkoxycarbonylcycloalkanones by Electrolysis of 1-Trimethylsiloxybicyclo[ $n.1.0$ ]alkanes

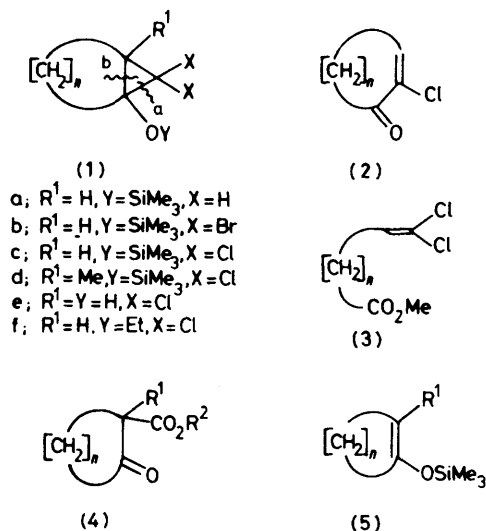
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**Summary** The  $\alpha$ -alkoxycarbonylcycloalkanones (**4**) were synthesized in 39–79% yields from the  $(n+3),(n+3)$ -dichloro-1-trimethylsiloxybicyclo[ $n.1.0$ ]alkanes (**1c**;  $n=4, 5,$  and  $10$ ) by electrolysis in alcohols in the presence 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<sup>1</sup> and homolytic

cleavage with iron(III) chloride at bond b.<sup>2</sup> 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.<sup>3</sup> In contrast, Schäfer *et al.* have found that anodic oxidation of (1f) affords the acyclic  $\omega$ -dichlorovinylidene esters (3;  $n = 4, 5, \text{ and } 6$ ), preferentially.<sup>4</sup> As part of our programme on development of electrochemical reactions, we have found a convenient method for the introduction of an alkoxy carbonyl group at the  $\alpha$ -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  $\beta$ -keto esters (4).<sup>5</sup>



A typical electrolysis procedure is as follows: a solution of (1c;  $n = 4$ ; 0.45 mmol),  $LiClO_4 \cdot 3H_2O$  (6.23 mmol), and  $Fe(NO_3)_3 \cdot 9H_2O$  (0.46 mmol) in MeOH (95 ml) was added to the anode compartment of an electrolysis cell.<sup>6</sup> The cathode compartment contained a solution of  $LiClO_4 \cdot 3H_2O$  (1.24 mmol) in MeOH (23 ml). The mixture was electrolysed with a constant current of 0.003 A/cm<sup>2</sup> terminal voltage 5 V (cell voltage *ca.* 1.3 V *vs.* SCE), using platinum

† 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<sup>-1</sup> (OH);  $\delta$  (CDCl<sub>3</sub>) 2.72 (s, 1H, OH).

<sup>1</sup> J. M. Conia and C. Girard, *Tetrahedron Letters*, 1973, 2767.

<sup>2</sup> Y. Ito, S. Fujii, and T. Saegusa, *J. Org. Chem.*, 1976, **41**, 2073.

<sup>3</sup> P. Amice, L. Blanco, and J. M. Conia, *Synthesis*, 1976, 196.

<sup>4</sup> M. Klehr and H. J. Schäfer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 247.

<sup>5</sup> L. Ruest, G. Blourin, and P. Deslongchamps, *Synth. Comm.*, 1976, **6**, 169 and references cited therein.

<sup>6</sup> S. Torii, H. Tanaka, and T. Okamoto, *Bull. Chem. Soc. Japan*, 1972, **45**, 2783.

TABLE. Yields of  $\alpha$ -alkoxycarbonylcycloalkanones (4) from (1c)<sup>a</sup> and (1d)<sup>a</sup>

$-[CH_2]_n-$ $n$	$\alpha$ -Alkoxy carbonylcycloalkanones (4) <sup>b</sup> $R^1$	$R^{2c}$	Yield, <sup>d</sup> %
4	H	Me	72
4	H	Et	77
5	H	Me	73
5	H	Et	97
10	H	Me	39 <sup>e</sup>
10	H	Et	48 <sup>e</sup>
4	Me	Me	56
4	Me	Et	61

<sup>a</sup> 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;  $n = 4, 5, \text{ and } 10$ ; 1d;  $n = 4$ ). <sup>b</sup> Ref. 5. <sup>c</sup>  $R^2$  refers to the alcohol (MeOH or EtOH) used as electrolysis solvent. <sup>d</sup> Based on isolated yields. <sup>e</sup> The low solubility of (1c;  $n = 10$ ) in alcohols suppresses the formation of (4;  $n = 10$ ).

electrodes (6 cm<sup>2</sup>) 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;  $n = 4, 5, \text{ and } 10$ ) 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;  $n = 4$ ).

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