## EXPERIMENTAL

<u>2-Phenyldimethylsiloxy-4,6-di(tert-butyl)phenol</u> was prepared according to Vasileiskaya et al. [5]. Fractionation in vacuum gave a product with bp 152-155°C (0.1 mm),  $n_D^{20}$  1.5212.

The kinetics studies were carried out in evacuated ampuls. The reaction was monitored relative to the loss of (III) and accumulation of (II) using a Tsvet 134 chromatograph with a thermal conductance detector. The IR spectra were taken on a UR-20 spectrophotometer.

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SYNTHESIS OF CYCLOPENTANE DERIVATIVES IN THE

CATHODIC ELECTROLYSIS OF COMPOUNDS WITH AN ACTIVATED

METHYLENE GROUP IN THE PRESENCE OF 1,4-DIBROMOBUTANE

V. I. Tatarinova, A. A. Vasil'ev, and V. A. Petrosyan UDC 541.135:542.91:547.514:547.412.24

The cathodic electrolysis of compounds with an activated methylene group in the presence of 1,4-dibromobutane leads to 1,1-disubstituted cyclopentanes.

In previous work [1], we have shown that the cathodic electrolysis of compounds with an activated methylene group (CAMG) in 1,2-dichloroethane leads to cyclopropane derivatives. In a continuation of this work, we studied the feasibility of the cathodic synthesis of five-membered alicyclic compounds upon the electrolysis of compounds with an activated methylene group in the presence of 1,4-dibromobutane.

#### EXPERIMENTAL

The electrolysis was carried out in a diaphragm cell. A 35 cm<sup>2</sup> sheet of platinum foil treated in concentrated nitric acid and annealed on a Bunsen burner served as the cathode. A  $2 \times 10$ -mm vitreous carbon plate served as the anode. The catholyte consisted of 37 ml ace-tonitrile, 3 ml 1,4-dibromobutane, 3 g Bu<sub>4</sub>NBr, and 5 mmoles CAMG [acetylacetone (I), malono-dinitrile (II), ethyl acetoacetate (III), ethyl cyanoacetate (IV), diethyl malonate (V), ethyl phenylacetate (VI), and phenylacetonitrile (VII)]. The anolyte consisted of 20 ml acetonitrile, 1.5 g Bu<sub>4</sub>NBr, and 2 ml cyclohexene used as a trap for the Br<sub>2</sub> formed. The electrolysis was carried out at 20°C with rapid stirring using a magnetic stirrer in a gal-vanostatic mode (I ~ 80 mA, Q ~ 2.2 F per mole starting CAMG). The catholyte was analyzed by gas-liquid chromatography during the electrolysis on a Chrom 5 chromatograph using a 2.4-m column packed with SE-30 on Chromaton. The yield of products (VIII) and (IX) in the electrolysis of (I) and (II) was determined using undecane as the internal standard. In the other cases, the chromatograms were calculated by internal normalization. Products (VIII)-(XIII) were identified by gas-liquid chromatography. The retention times were compared with those

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TABLE 1. Yield of Cyclopentane Derivatives of  $CH_2XY$ (C = 0.125 M) in the Presence of  $Br(CH_2)_4Br$  (C = 0.625 M) in an Amperostatic Regime on a Platinum Cathode in Acetonitrile Containing  $Bu_4NBr$ 

Starting compound	x	Y	рК <sub>а</sub> [7, 8]	Conver- sion,* %	Products	Analytical yield, %	
						current yield	material yield**
(1)	Ac	Ac	9	100	(VIII)		38
άĎ	CN	CN	11	100	(IX)	85	100
$(\mathbf{\hat{1}1})$	Ac	COOEt	11	100	(X)	85	100
(1V)	CN	COOEt	13	100	(X1)	90	100
(V)	COOEt	COOEL	15	100	(XII)	90	100
(VII)	CN	$C_{e}H_{5}$	21	50	(XIII)	45	50
(VI)	COOF	C <sub>6</sub> H <sub>5</sub>	>21	0	No reaction		

"For Q - 2.2 F/mole.

\*\*Relative to CAMG taken.

for authentic samples. In the case of CAMG (III)-(V), the structure of the electrolysis products was additionally confirmed using PMR spectra, which coincided with those described by Zefirov et al. [2]. For this purpose, the catholyte was diluted with a two-fold volume of water and extracted with ether. The extracts were dried over calcium chloride and distilled. Cyclopentane derivatives (X)-(XII) were purified to remove the accompanying bromides by chromatography on alumina.

<u>Diethyl 4-bromobutylmalonate (XIV)</u> was isolated from the catholyte of the electrolysis of diethyl malonate (V) (1 F/mole was passed), bp 135°C (1 mm). PMR spectrum ( $\delta$ , ppm): 1.23 t (6H, CH<sub>3</sub>), 1.49 m (2H, CH<sub>2</sub>), 1.89 m (2H, CH<sub>2</sub>), 1.92 m (2H, CH<sub>2</sub>), 3.30 t (1H, <sup>3</sup>J = 7.3 Hz, CH), 3.39 t (2H, <sup>3</sup>J = 6.6 Hz, CH<sub>2</sub>Br), 4.19 q (4H, OCH<sub>2</sub>).

### RESULTS AND DISCUSSION

The electrolysis of CAMG (I)-(V) and (VII) on a platinum cathode in the presence of 1,4-dibromobutane leads to cyclopentane derivatives. The formation of these derivatives may be described by a scheme analogous to that described in our previous work [1] for the electrolytic synthesis of cyclopropane derivatives.

$$CH_2XY + \bar{e} \longrightarrow \bar{C}IIXY + \frac{1}{2}H_2 \tag{1}$$

 $\bar{C}HXY + Br(CH_2)_4Br \longrightarrow Br(CH_2)_4CHXY + Br^-$ (2)

 $Br(CH_2)_4 CHXY + \bar{e} \longrightarrow Br(CH_2)_4 \bar{C}XY + \frac{1}{2}H_2$ (3)

The possibility of cleavage of the C-H bond in the electrolysis of CH-acids on platinum, iron, nickel, and graphite cathodes in a nonaqueous medium (steps (1) and (3)) has been established in previous work [3-5]. The subsequent reactions of the generated carbanions presumably proceed through nucleophilic substitution reactions (steps (2) and (4)).

In the electrolysis of CAMG (I)-(IV) and (VII), we observed the gradual loss of the starting compounds and accumulation of the corresponding cyclopentane derivatives (VIII)-(XI) and (XIII). However, in the case of diethyl malonate (V), precursor  $Br(CH_2)_4CH(CO_2Et)_2$  (XIV), which is the product of the initial 4-bromobutylation of the anion of the starting CAMG, was detected in addition to cyclopentane derivative (XII). The maximum current yield (~50%) for

(XIV) was achieved upon the passage of ~lF/mole. The amount of (XIV) decreases upon further electrolysis and only the cyclopentane derivative is present in the catholyte for Q = 2.2 F/mole. These results, which support the proposed mechanism, indicate the stepwise formation of the five-membered ring in these reactions with the formation of  $Br(CH_2)_4CHXY$  compounds as intermediates.

The dependence of the current yield of cyclopentane derivatives (VIII)-(XIII) on the CH-acidity of the starting CAMG (I)-(VII) has the same tendency as in the electrolysis of cyclopropane derivatives [1]. The product yield is greatest for medium  $pK_a$  values (~11-15) and reaches 85-90%. The anions of stronger acids have less nucleophilicity, while the reduction of the dihaloalkane competes efficiently with cleavage of the C-H bond in the reduction of weaker acids. Each of these factors has a negative effect on the yield of the desired product. Thus, ethyl phenylacetate (VI), which has low acidity, does not undergo any visible change during the electrolysis (Table 1).

We note that, on the whole, the yield of the cyclopentane derivatives is significantly greater than for the cyclopropane derivatives [1]. This discrepancy is related to the greater difficulty in reducing 1,4-dibromobutane in comparison with 1,2-dichloroethane, in which the vicinal halogen atoms are relatively easily lost on the cathode with the formation of ethylene [6]. This process, which competes with reduction of the CH-acid (see above), decreases the yield of the cyclic product.

Thus, the cathodic electrolysis of several compounds with an activated methylene group in the presence of 1,4-dibromobutane may be used for the preparation of 1,1-disubstituted cyclopentanes in addition to various chemical reactions [2].

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