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ELECTROCHEMICAL OXIDATION OF KETONES IN METHANOL IN THE PRESENCE OF ALKALI METAL BROMIDES

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Abstract: Electrochemical oxidation of methyl ketones in methanol in the presence of alkali metal bromides affords methyl carboxylates. Benzyl alkyl ketones are transformed under similar conditions into methyl 3-phenylalkanoates, while ketones lacking α-benzyl or α-methyl group are oxidized into α-hydroxyketals.

INTRODUCTION

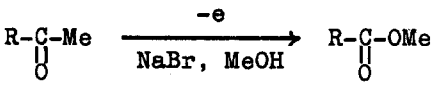
Electrochemical oxidation of ketones results usually in a mixture of acids, saturated and unsaturated hydrocarbons, carbon oxide and dioxide[1-4]. Remote oxidative functionalization of ketones was observed when electrooxidation has been carried out in acetonitrile or trifluoroacetic acid as a result of subsequent transformation of an initially produced cation-radical $R^1R^2C{=}O^{+\cdot}$ [5,6]. In certain cases selective electrooxidation takes place. Thus, electrolysis of acetophenones in DMSO in the presence of CuBr affords arylglyoxals[7], electrooxidation of cyclohexanone in the methanol in the presence of KI gives 2,2-dimethoxycyclohexanol[8], and aryl alkyl ketones give methyl 2-arylalkanoates being electrolysed in methyl orthoformate in the presence of iodides[9].

Continuing our studies on electrooxidation of organic compounds in the presence of halides as mediators we have accomplished electrochemical oxidation of ketones in methanol in the presence of bromides.

RESULTS AND DISCUSSION

Electrocatalytic haloform reaction

We have established[10] that electrooxidation of methyl ketones in methanol in the presence of alkali metal bromides in an undivided cell led to the corresponding methyl esters (Table 1):



1a-g

a R = Ph
b R = 4-MeC_6H_4
c R = 4-$MeOC_6H_4$
d R = 1-naphthyl

2a-g

e R = $Me(CH_2)_5$
f R = i-Pr
g R = PhCH=CH

Table 1. Electrooxidation of methyl ketones 1a-g in methanol in the presence of NaBr[a)]

Entry	Substrate	[NaBr] : [1] (molar ratio)	Conversion (%)	Yield of ester 2 (%), based on 1 converted
1	1a	3.00	100	71
2	1a	1.50	100	74
3	1a	0.75	100	63
4	1a	0.35	100	64
5	1a	0.20	92	42
6	1a	0.10	85	15
7	1b	1.50	93	83
8	1c	1.50	89	85
9	1d	1.50	100	88
10	1e	1.50	97	62
11	1f	1.50	78	67[b)]
12	1g	1.50	98	61[c)]

a) 20 mmol of 1 in 20 ml of methanol, Pt-anode, Cu-Zn (60:40)-cathode, current density 220 mA/cm^2, amount of electricity passed 7.5 F/mol, 30° C.

b) Determined by GLC.

c) 5 F/mol

Sodium bromide is the optimal electrolyte. Its replacement with NaI or KBr resulted in decrease in the yield of 2a to 30-50%. In the presence of NaCl the yield of 2a was 15%, no methyl benzoate was produced in the presence of NaOMe or $NaClO_4$, the conversion of acetophenone (1a) being 70-80%. In the last three examples the main process was the condensation of 1a as well as its polycondensation with formaldehyde produced upon oxidation of methanol. The pronounced oxidation of methanol in formaldehyde upon electrolysis in the presence of NaCl was observed as well as formation of products of condensation and polycondensation of formaldehyde with substrate[11].

The optimum electrolyte-to-substrate molar ratio was found to be 1.50 (1.5:1.0). Methyl benzoate (2a) was produced in considerable yields (64 and 42%) at lower electrolyte proportions (0.35 and 0.20), whereas at the 0.10 ratio it drops to 15% (Table 1, entries 4-6). The process is to small extent sensitive to the material of electrodes, methyl benzoate (2a) was formed in considerable yield with Pt or C as an anode and Ni or C as a cathode.

The results obtained as well as the direct observation of the formation of bromine at anode allow to suggest the following reaction mechanism:

anode: $6\ Br^- - 6e \longrightarrow 3\ Br_2$ (1)

cathode: $6\ MeOH + 6e \longrightarrow 6\ MeO^- + 3\ H_2$ (2)

in solution: $R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Me + 3\ Br_2 \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CBr_3 + 3\ H^+ + 3\ Br^-$ (3)

1a-g

$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CBr_3 + MeO^- \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMe + CBr_3^-$ (4)

2a-g

The formation of bromoform was established at the end of the reactions (Table 1, entries 1-4), its content decreased from 0.2 to 0.065 molar equivalents as the content of NaBr diminished from 3 to 0.35 molar equivalents. It then follows that the amount of NaBr to be used under conditions specified should not be less that 0.2 equivalent with respect to substrate. This is in good accord with the experimental data (Table 1, entries 5,6).

Accumulation of bromoform in the reaction mixture can result in its cathode reduction or its reaction with methoxide-ions, both processes ensuring regeneration of Br^--ions. In a special experiment it was

established that interaction of $CHBr_3$ (20 mmol) with NaOMe (3 equiv.) in MeOH (20 ml) at 30° for 4 hr (usual electrolysis time) results in formation of methyl orthoformate in a yield of 100% for bromoform converted, the conversion being 80%. Electrolysis of $CHBr_3$ (20 mmol) in the presence of NaBr (1.5 equiv.) at 30° for 4 hr (conditions of entry 2, Table 1) resulted in 45%-conversion of $CHBr_3$, the yield of methyl orthoformate being 15%. Taking into account these data as well as the fact that methyl orthoformate is formed in 65% yield in entry 2 (Table 1), one may conclude that the principal pathway of regeneration of Br^--ions is the interaction of bromoform with methoxide-ions:

$$CBr_3^- + MeOH + 2\ MeO^- \longrightarrow HC(OMe)_3 + 3\ Br^- \qquad (5)$$

Summing up the above equations (1) - (5) we have a general equation of the process:

$$\underset{\underline{1a\text{-}g}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Me} + 4\ MeOH \xrightarrow[NaBr\text{-}MeOH]{electrolysis} \underset{\underline{2a\text{-}g}}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMe} + HC(OMe)_3 + 3\ H_2$$

The electrocatalytic process found by us is applicable to oxidation of both aromatic and aliphatic methyl ketones. Oxidation of 2-octanone (1e) affords, alongside with 2e, 29% of 2,2-dimethoxy-3-octanol (3). The presence of α-ramification in an aliphatic ketone, as in the case of isopropyl methyl ketone (1f) favours selectivity of the main process. This is in good agreement with the data[12] on α-bromination of unsymmetrical ketones with bromine in methanol, which is directed preferentially at the less substituted C-atom. Thus, α-bromination of the methyl group in 2-butanone amounts to 70% versus 30% bromination of the methylene group, whereas for isopropyl methyl ketone it is as high as 95% under the same conditions[12].

The elaborated electrooxidation was successfully applied to unsaturated ketone, benzylideneacetone (1g) (entry 12, Table 1). With mesityl oxide as the starting ketone no product of the electrocatalytic haloform reaction, viz. methyl α,α-dimethylacrylate, could be isolated as it undergoes cathode reductive coupling under reaction conditions to produce a mixture of three possible dimers.

Thus, we have developed an electrocatalytic variant of haloform reaction, the simplest procedure to prepare carboxylic acids or esters from methyl ketones[13-15]. The much higher ease of introduction of an acetyl group into an aromatic ring compared to carboxyl group determines especial value of this method for synthesis of aromatic acids and derivatives thereof.

Electrochemically induced Favorskii rearrangement

Electrolysis of benzyl ketones under conditions, which cause electrocatalytic haloform reaction of methyl ketones, results in their transformation into methyl 3-phenylalkanoates. This process involves Favorskii rearrangement (Table 2):

$$PhCHR^1C(=O)CH_2R^2 \xrightarrow[NaBr,\ MeOH]{-e} PhCHR^1CHR^2C(=O)OMe$$

4a-c 5a-c

a $R^1=R^2=H$; b $R^1=H$, $R^2=Me$; c $R^1=Me$, $R^2=H$

Table 2. Electrooxidation of benzyl ketones 4a-c in methanol in the presence of sodium halides[a)]

Substrate	Electrolyte	[Electrolyte]:[4]	Products, yield % on the starting 4[b)]
4a	NaBr	1.50	5a, 52; PhCH(OH)CH(OMe)$_2$Me (6), 45
4a	NaBr	0.75	5a, 33; 6, 57
4a	NaBr	0.35	5a, 32; 6, 54
4a	NaI	1.50	5a,[c)] 56; 6,[c)] 25
4b	NaBr	1.50	5b, 54; PhCH(OH)CH(OMe)$_2$Et (7), 22
4c	NaBr	1.50	5c, 60; PhCHMeC(=O)OMe (8), 37

a) 20 mmol of 4 in 20 ml of methanol, Pt-anode, Cu-Zn (40:60) cathode, current density 220 mA/cm^2, amount of electricity passed 7.5 F/mol, 30° C.

b) Determined by GLC, conversion of 4 100%.

c) Conversion 81%, yield based on 4a converted.

Upon electrolysis of 4a,b are formed esters 5a,b and α-hydroxyketals 6 and 7. As to 4c, under conditions specified it gives rise to 5c and to the product of electrochemical haloform reaction, methyl 2-phenylpropanoate (8).

Decrease in amount of NaBr results in decrease in the yield of 5a and somewhat large production of 6. The use of NaI as the electrolyte allows to obtain 5a in a considerable yield, whereas upon replacement of NaBr for NaCl the major direction of a reaction, like for methyl ketones, is the condensation of 4a.

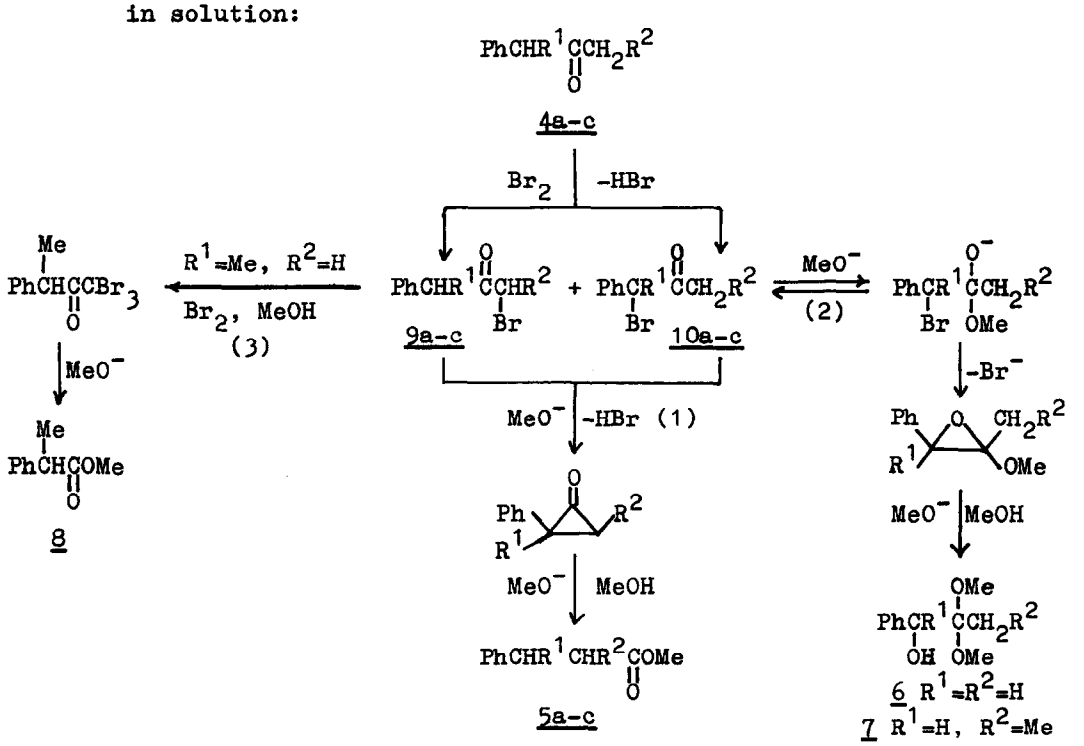
Bromination of 4a with elemental bromine in methanol is known to affect both α-C-atoms at about the same proportion[12]. Treatment of 1-chloro-3-phenyl-2-propanone with NaOMe gives 5a, while 1-chloro-1-phenyl-2-propanone gives under these conditions a mixture of 6 and 5a in yields of 81 and 13% [16,17].

On the basis of the experimental results and literature data the following mechanism for the electrochemical transformation of benzyl ketones is suggested:

$$\text{anode: } 2\,Br^- - 2e \longrightarrow Br_2$$

$$\text{cathode: } 2\,MeOH + 2e \longrightarrow 2\,MeO^- + H_2$$

in solution:



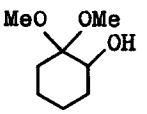
Scheme

The role of the main precursors of 5a-c is played by α-bromoketals 9a-c, the mobility of the benzylic proton in which enables facile elimination of HBr under the action of methoxide-ion (Scheme, path 1). α-Bromoketones 10a,b are converted principally into ketals 6,7 (Scheme, path 2) according to a mechanism similar to that suggested[8,17]. In the case of 4c, for the steric reasons[12], it is 9c that is preferentially formed at the first stage. Sterically hindered cyclization of 9c allows a competitive process to take place, viz., exhaustive bromination of the terminal methyl group of 4c to give finally 8c, the product of haloform reaction (Scheme, path 3).

Electrochemical oxidation of alkyl aryl ketones and cyclohexanone

Provided the ketone, which can be α-brominated, does not contain either α-methyl or benzyl group it is electrooxidized in methanol in the presence of NaBr to give selectively α-hydroxyketals (Table 3).

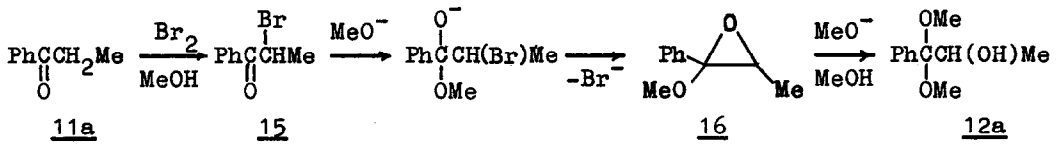
Table 3. Electrochemical oxidation of ketones into α-hydroxyketals in methanol in the presence of NaBr[a)]

Ketone	Amount of electricity passed F/mol	Conversion (%)	Product and yield (%) based on ketone converted
$PhC(=O)CH_2R$			$PhC(OMe)_2CHR$ (OH)
11a R=Me	7.5	100	12a R=Me, 78
11b R=Pr	7.5	100	12b R=Pr, 74
11c R=i-Pr	10.0	85	12c R=i-Pr, 73
 13	3.5	100	 14 79

a) 20 mmol of ketone, 30 mmol of NaBr in 20 ml of methanol, Pt-anode, Cu-Zn (60:40) cathode, current density 220 mA/cm^2, 30° C.

Bromination of ketones 11a-c affects selectively α-methylene group, two α-C-atoms being equivalent in the symmetrical cyclohexanone 13. Therefore transformation along the path 1 (Scheme) become impossible

for the ketones 11a-c. It is not realised for 13, possibly, due to insufficient mobility of the proton in α-methylene groups of 13 compared to that of the benzylic proton in benzyl ketones 4a-c. Thus upon electrolysis of 11a-c and 13 under conditions specified in Table 3 a process is realised selectively which is close to that given in the Scheme (path 2) and, for instance, for propiophenone (11a) can be rewritten as follows:



11a 15 16 12a

Formation of the oxirane 16 took place when 15 was treated with dry NaOMe in ether[18], interaction of the isolated 16 with NaOMe in methanol afforded 12a[18].

α-Hydroxyketals of aryl ethyl ketones are convenient starting compounds in the synthesis of pharmacologically active 2-arylpropionic acids[19-21].

Thus, electrolysis of ketones in methanol in the presence of NaBr can produce under identical conditions, depending on the structure of ketone, the products of haloform reaction or electrochemically induced Favorskii rearrangement, or α-hydroxyketals. In the course of each of the processes of electrooxidative transformation of ketones presented here the bromide ions are regenerated thereby functioning as mediators.

EXPERIMENTAL

G.l.c. analyses were carried out on Chrom-5 chromatograph fitted with a flame-ionization detector. Glass columns used were 3000×3mm with 3% XE-60 on Inerton Super (0,13-0,16 mm), with 5% SE-Superphase on Inerton Super (0,16-0,20 mm), and with 5% OV-220 on Chromaton N-Super (0,13 - 0,16 mm). ^{1}H-NMR and ^{13}C-NMR spectra were run for solutions in $CDCl_3$ and recorded with a "Bruker AM-300" (300 MHz) spectrometer. Chemical shifts are presented in δ scale with tetramethylsilane (TMS) used as internal standard.

NaBr and NaI were reagent grade samples used after additional drying in vacuo.

Initial ketones were reagent samples purified by distillation before utilisation.

Electrolysis of ketones in methanol in the presence of sodium bromide. General procedure. A solution of ketone (20 mmol) and NaBr (2-60 mmol) in methanol (20 ml) was electrolysed under magnetic stirring in an undivided cell with external cooling, equipped with Pt-anode (4.5 cm^2) and Cu-Zn (60:40) cathode (4.5 cm^2) at 30°C under constant current density 220 mA/cm^2 until the quantity of electricity indicated in Tables 1-3 was passed. After completion of the reaction and removal of methanol the mixture was extracted with ether (3x30 ml). The combined extracts were washed with water (2x30 ml), dried with Na_2SO_4, evaporated and residue was distilled.

Methyl benzoate 2a, methyl 4-methylbenzoate 2b, methyl 4-methoxybenzoate 2c, methyl heptanoate 2e, methyl iso-butanoate 2f, and methyl cinnamate 2g were identified by comparison with standard samples.

Methyl 1-naphthalenecarboxylate 2d. Yield 88%; b.p. 93-94°C/0.1 torr; ^{1}H-NMR: 4.01 (s, 3H, OCH_3), 7.5-8.3 (m, 7H, aryl-H).

On completion of electrolysis of 1a bromoform was detected in reaction mixtures by g.l.c. analysis in quantities: 4 mmol (Table 1, entry 1), 2.9 mmol (Table 1, entry 2), 1.8 mmol (Table 1, entry 3), 1.3 mmol (Table 1, entry 4). Methyl orthoformate was also identified (13 mmol, yield 65%, Table 1, entry 2).

Interaction of bromoform with sodim methoxide in methanol. Bromoform (10 mmol) was added to a solution of Na (30 mmol) in 20 ml of methanol. The reaction mixture was stirred for 4 hr at 30°, then analysed by g.l.c. Conversion of bromoform 80%, yield of methyl orthoformate 8 mmol (100% based on converted $CHBr_3$).

Electrolysis of bromoform in methanol in the presence of NaBr. A solution of $CHBr_3$ (20 mmol) and NaBr (30 mmol) in 20 ml of methanol was electrolysed according to general procedure. After 7.5 F/mol of electricity was passed the reaction mixture was analysed by g.l.c. Conversion of bromoform 45%, yield of methyl orthoformate 3 mmol (15%).

2,2-Dimethoxy-3-octanol 3. Yield 29%; b.p. 108-110°/12 torr; ^{1}H-NMR: 0.83 (t, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.20-1.65 (m, 8H, CH_2), 2.18 (s, 1H, OH), 3.17 (s, 3H, OCH_3), 3.19 (s, 3H, OCH_3), 3.69 (m, 1H, CH); ^{13}C-NMR: 13.88 (q), 16.02 (q), 22.31 , 23.09 , 29.24 and 31.44 (t), 47.95 (q), 48.32 (q), 72.28 (d), 102.62 (s).

Methyl 3-phenylpropanoate 5a. Yield 52%; b.p. 122-124°/14 torr; ^{1}H-NMR: 2.67 (t, 2H, CH_2), 2.99 (t, 2H, CH_2), 3.70 (s, 3H, OCH_3), 7.28 (m, 5H, C_6H_5).

Methyl 2-methyl-3-phenylpropanoate 5b. Yield 54%; b.p. 59-60°/0.07 torr; ^{1}H-NMR: 1.11 (d, 3H, CH_3), 2.67 (d, 2H, CH_2), 2.99 (m, 1H, CH), 3.60 (s, 3H, OCH_3), 7.32 (m, 5H, C_6H_5).

Methyl 3-phenylbutanoate 5c. Yield 60%; b.p. 130-132°/45 torr; ^{1}H-NMR: 1.32 (d, 3H, CH_3), 2.62 (m, 2H, CH_2), 3.31 (m, 1H, CH), 3.64 (s, 3H, OCH_3), 7.28 (m, 5H, C_6H_5).

2,2-Dimethoxy-1-phenyl-1-propanol 6. Yield 45%; m.p. 57-59°; ^{1}H-NMR: 1.04 (s, 3H, CH_3), 2.71 (s, 1H, OH), 3.24 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 4.80 (s, 1H, CH), 7.12-7.58 (m, 5H, C_6H_5); ^{13}C-NMR: 16.28 (q), 48.01 (q), 48.57 (q), 73.16 (d), 102.70 (s), 126.95 (d), 127.05 (d), 127.31 (d), and 139.58 (s).

2,2-Dimethoxy-1-phenyl-1-butanol 7. Yield 22%; b.p. 75-77°/0.08 torr; ^{1}H-NMR: 0.98 (t, 3H, CH_3), 2.01 (q, 2H, CH_2), 2.90 (s, 1H, OH), 3.27 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 4.89 (s, 1H, CH), 7.10-7.55 (m, 5H, C_6H_5).

Methyl 2-phenylpropanoate 8. Yield 37%; b.p. 122-124°/45 torr; ^{1}H-NMR: 1.53 (d, 3H, CH_3), 3.68 (s, 3H, OCH_3), 3.77 (q, 1H, CH), 7.28 (m, 5H, C_6H_5).

1,1-Dimethoxy-1-phenyl-2-propanol 12a. Yield 78%; b.p. 69-70°/0.05 torr; ^{1}H-NMR: 0.93 (d, 3H, CH_3), 2.68 (s, 1H, OH), 3.18 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 4.09 (q, 1H, CH), 7.15-7.56 (m, 5H, C_6H_5); ^{13}C-NMR: 16.41 (q), 49.18 (q), 49.80 (q), 70.51 (d), 103.50 (s), 126.63 (d), 127.56 (d), 128.11 (d), and 137.27 (s).

1,1-Dimethoxy-1-phenyl-2-pentanol 12b. Yield 74%; b.p. 80-82°/0.05 torr; ^{1}H-NMR: 0.83 (t, 3H, CH_3), 1.19-1.57 (m, 4H, CH_2), 2.58 (s, 1H, OH), 3.22 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.93 (m, 1H, CH), 7.16-7.58 (m, 5H, C_6H_5). ^{13}C-NMR: 13.97 (q), 19.44 (t), 32.88 (t), 49.18 (q), 49.83 (q), 74.12 (d), 103.43 (s), 127.66 (d), 127.77 (d), 127.92 (d), and 137.62 (s).

1,1-Dimethoxy-3-methyl-1-phenyl-2-butanol 12c. Yield 62%; b.p. 98-100°/0.3 torr; ^{1}H-NMR: 0.69 (d, 3H, CH_3), 0.88 (d, 3H, CH_3), 1.45 (m, 1H, $CHMe_2$), 2.67 (s, 1H, OH), 3.23 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 3.73 (m, 1H, CHOH), 7.16-7.60 (m, 5H, C_6H_5); ^{13}C-NMR: 17.59 (q), 21.08 (q), 28.65 (d), 49.88 (q), 50.37 (q), 78.59 (d), 103.40 (s), 127.21 (d), 127.76 (d), 127.96 (d), and 138.18 (s).

2,2-Dimethoxycyclohexanol 14. Yield 79%; b.p. 38-39°/0.08 torr; ^{1}H-NMR: 1.20-1.75 (m, 8H, CH_2), 2.23 (s, 1H, OH), 3.14 (s, 3H, OCH_3), 3.16 (s, 3H, OCH_3), 3.75 (m, 1H, CH); ^{13}C-NMR: 19.57 (t), 22.04 (t), 27.77 (t), 29.07 (t), 47.31 (q), 47.95 (q), 68.04 (d), 100.55 (s).

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