BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 162—168 (1967)

Electrochemical Syntheses. IV. The Homolytic Methoxylation and Ethoxylation of Olefins by the Anodic Oxidation of Methanol and Ethanol*[1]

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(Received May 4, 1966)

The electrochemical oxidation of methanol and ethanol in the presence of *trans*-stilbene, *cis*-stilbene, norbornene, and styrene has been studied. The major gaseous and nongaseous products have been identified and determined, and the corresponding dimethoxylated derivatives and diethoxylated derivatives have been obtained in fairly high yields. The main path by which these products may have arisen has been discussed, and the stereochemistry of the addition of methoxy radicals to stilbene has been discussed. Particular attention has been given to the possibility that the main product arises from the anodic oxidation of an intermediate radical to a carbonium ion.

In the preceding paper[1] of this series,[1-3] the present authors have shown that the anodic oxidation of methanol in the presence of some arylated olefins produced α, β-dimethoxylated derivatives, and that the reaction involved an intermediate radical which was formed by the addition of a methoxy radical to olefinic double bonds.

[*1] A part of this work appeared in *Tetrahedron Letters*, **1963**, 1409.

1) T. Inoue and S. Tsutsumi, This Bulletin, **38**, 661 (1965).

2) T. Inoue, K. Koyama and S. Tsutsumi, *ibid.*, **37**, 1597 (1964).

3) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka and S. Tsutsumi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1659 (1963).

The present investigation was undertaken to provide additional information about the addition of methoxy radicals to olefinic double bonds, and also to sudy the stereochemistry of this reaction. For this purpose, *trans*-stilbene, *cis*-stilbene, and norbornene were chosen as the starting materials. Styrene was used in the anodic oxidation of ethanol.

Results and Discussion

The Addition of Methoxy Radicals to Stilbenes. According to the procedure previously employed for alkylated aromatic hydrocarbons,[2,3] the electrolysis was carried out by using two platinum foil electrodes in a cylindrical glass cell. The current was controlled at nearly 0.3 A (5—6 V), and the temperature was kept at 35°C.

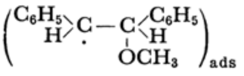
The electrolysis of methanol containing sodium methoxide in the presence of *trans*-stilbene (I) for 45 hr gave *dl*-hydrobenzoin dimethyl ether (II) in a 44% yield based on the *trans*-stilbene used, along with *meso*-hydrobenzoin dimethyl ether (III) (20%), bibenzyl (IV) (a trace), and unidentified oily products (14%); 2% of *trans*-stilbene was recovered.

On the other hand, *meso*-hydrobenzoin dimethyl ether (III) (26.3%), *dl*-hydrobenzoin dimethyl ether (II) (17.5%), bibenzyl (IV) (6.5%), and unidentified oily products (12.5%) were obtained from *cis*-stilbene (V) after 75 hr; 3.8% of *cis*-stilbene was then recovered. The reaction conditions and the yields of products are summarized in Table 1.

Since, as has been shown previously,[1-3] the methoxy radical may be initially produced as an intermediate in these reaction systems, it may be expected that the reaction of the methoxy radical with stilbenes takes place in the first step of the reaction:

$$CH_3O^- \xrightarrow[-e]{\text{anode}} (CH_3O\cdot)_{ads} \qquad (1)$$

$$(CH_3O\cdot)_{ads} + \underset{(I)}{C_6H_5CH{=}CHC_6H_5} \rightarrow$$

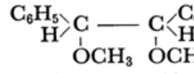


$$\left(\begin{matrix}C_6H_5\\H\end{matrix}\!>\!\dot{C}-C\!<\!\begin{matrix}C_6H_5\\H\end{matrix}\atop \qquad\quad |\atop \qquad\quad OCH_3\right)_{ads} \qquad (2)$$

(VI)

Thus, the formation of *meso*- or *dl*-hydrobenzoin dimethyl ether (II or III) may occur by two alternative reaction paths:

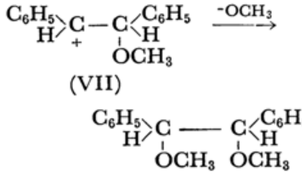
In the first, the benzylic intermediate radical (VI) reacts with another methoxy radical to give the dimethyl ether (II or III), since the environment around the electrode might have a particularly high concentration of the methoxy radical (Eq. (3)):



$$(VI) + (CH_3O\cdot)_{ads} \rightarrow \begin{matrix}C_6H_5\\H\end{matrix}\!>\!\underset{OCH_3}{\underset{|}{C}} - \underset{OCH_3}{\underset{|}{C}}\!<\!\begin{matrix}C_6H_5\\H\end{matrix} \qquad (3)$$

(*meso*- or -*dl*)
III II

In the second, the intermediate radical (VI) may be oxidized to the carbonium ion (VII) to give the solvolysis product (II or III) (Eq. (4));



$$(VI) \xrightarrow[\text{anode}]{-e} \begin{matrix}C_6H_5\\H\end{matrix}\!>\!\overset{}{\underset{+}{C}} - \underset{OCH_3}{\underset{|}{C}}\!<\!\begin{matrix}C_6H_5\\H\end{matrix} \xrightarrow{^-OCH_3}$$

(VII)

$$\begin{matrix}C_6H_5\\H\end{matrix}\!>\!\underset{OCH_3}{\underset{|}{C}} - \underset{OCH_3}{\underset{|}{C}}\!<\!\begin{matrix}C_6H_5\\H\end{matrix} \qquad (4)$$

(*dl*- or *meso*-)
II III

Such carbonium ions as intermediates in the Kolbe electrolysis have been reported by many workers.[4-8] It is known that, in the Kolbe electrolysis, electrolytically-generated benzyl radiacls are oxidized with greater ease.[8] The rearranged product which may result from the formation of a carbonium ion was obtained in our reaction system using norbornene, as will be described later. Thus, it seems that the second reaction path (Eq. (4)) may take place in preference to the first path (Eq. (3)).

Of particular interest is the fact that the addition of the methoxy radical to stilbenes proceeds stereochemically under these conditions. Table 1 shows that the electrolysis of *trans*-stilbene gives *dl*-hydrobenzoin dimethyl ether (II) in a yield about 2 times that of the *meso*-isomer (III); on the contrary, *meso*-hydrobenzoin dimethyl ether (III) was obtained from *cis*-stilbene in a yield about 1.5 times that of the *dl*-isomer (II). These results indicate that *cis*-addition to stilbenes takes place in preference to *trans*-addition under these conditions. The stereochemical picture of these addition reactions is shown in Fig. 1.

Smith and Gilde[9] explained that the stereospecificity in the Kolbe electrolysis might be due to the addition of an electrolytically-produced radical to the conjugated-diene adsorbed on the electrodes. In our experiments, it seems that the stereospecificity may be due to the attack of an adsorbed methoxy radical on the adsorbed stilbene molecule, immediately followed by the anodic oxidation of the

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[4] E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

[5] C. Walling, "Free Radicals in Solution," John Wiley & Sons, N. Y. (1957), p. 579.

[6] W. J. Koehl, *J. Am. Chem. Soc.*, **86**, 4686 (1964).

[7] F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

[8] W. A. Bonner and F. D. Mango, *ibid.*, **29**, 430 (1964).

[9] W. B. Smith and H. G. Gilde, *J. Am. Chem. Soc.*, **81**, 5325 (1959).

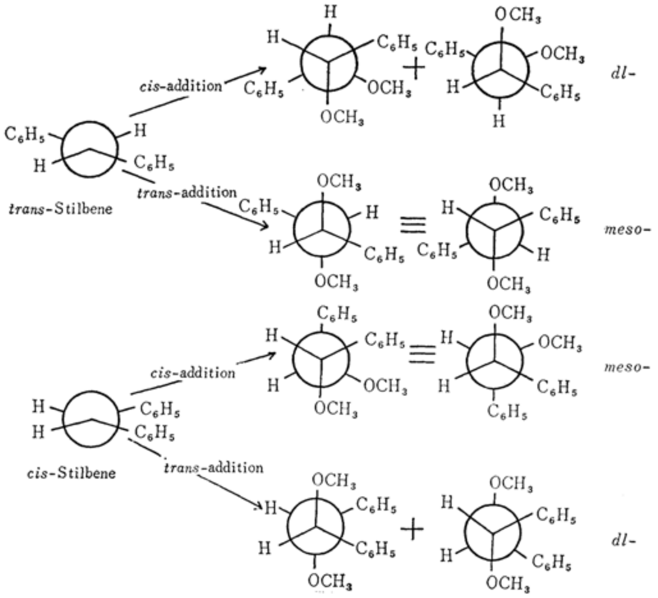
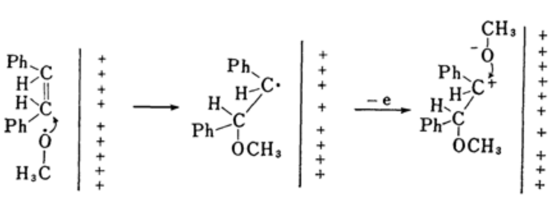


Fig. 1. Stereochemistry of addition reaction of methoxy radicals to stilbenes.

adsorbed intermediate radical to form a carbonium ion. The ion is then attacked by the methoxide ion to give the solvolysis product, as is shown below:



Bibenzyl (IV) may be produced by the cathodic reduction of stilbenes, since ethylene was easily reduced under these conditions.[10]

$$Na^+ \xrightarrow[\text{cathode}]{+e} Na$$

$$Na + CH_3OH \rightarrow CH_3ONa + H\cdot\ (H_2)$$

$$2H\cdot\ (H_2) + C_6H_5CH{=}CHC_6H_5 \rightarrow \underset{\text{IV}}{C_6H_5CH_2CH_2C_6H_5}$$

Electrolysis in the Presence of an Electrolyte. When the anodic oxidation of methanol containing ammonium perchlorate as an electrolyte was carried out in the presence of *trans*-stilbene, benzaldehyde was obtained as the main product, along with small amounts of unidentified miscellaneous products. No hydrobenzoin dimethyl ether was detected among the reaction products. When ammonium bromide was used, *erythro*-stilbene dibromide (VIII) was obtained as the main product, as well as α-methoxy-β-bromo-1, 2-diphenyl ethane (IX) and a small amount of *meso*-hydrobenzoin dimethyl ether (III).

These results, shown in Table 2, indicate that sodium methoxide is a good electrolyte for the anodic methoxylation of stilbene under these conditions. Previously, Clauson-Kaas and his co-workers[11–13] reported that the bromine which is formed during the electrolysis of ammonium bromide solutions reacts immediately with furan-compounds and methanol to give the methoxylated products and hydrogen bromide. However, in the absence of an other electrolyte, the anodic oxidation of methanol containing sodium methoxide gave the dimethyl ether derivatives in good yields, as is shown in Table 2.

The Addition of Methoxy Radicals to Norbornene. In order to examine the possibility of the formation of carbonium ions as an intermediate under these conditions, the electrolysis of methanol was carried out in the presence of norbornene (X). If rearranged products were obtained, the formation of a carbonium ion as an intermediate would be indicated.

The anodic oxidation of methanol in the presence of norbornene gave *exo-syn*-2, 7-dimethoxy bicyclo(2, 2, 1) heptane (XI) as the main product, along with *exo*-2-methoxy bicyclo(2, 2, 1) heptane (XII) and two unidentified dimethoxylated derivatives; it gave no *cis*-2, 3-dimethoxy bicyclo-(2, 2, 1) heptane.

The formation of the rearranged product, *exo-syn*-2, 7-dimethoxy bicyclo(2, 2, 1) heptane (XI),

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[10] Unpublished works.

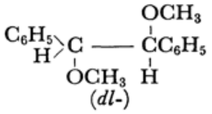
[11] N. Clauson-Kaas, F. Limborg and K. Glens, *Acta Chem. Scand.*, **6**, 531 (1952).

[12] N. Clauson-Kaas, F. Limborg and P. Dietrich, *ibid.*, **6**, 545 (1952).

[13] N. Clauson-Kaas and Z. Tyle, *ibid.*, **6**, 667 (1952).

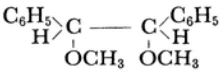
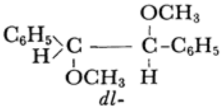
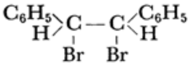
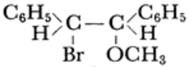
TABLE 1. ANODIC METHOXYLATION OF STILBENES

Expt. No.	$C_6H_5CH=CHC_6H_5$ g	CH_3OH m*l*	Metallic sodium g	Condition Volt	A	Electrode (distance)	hr	A·hr	Temp. °C
1	*trans*- 5.0	150	2.0	5—6	0.3	2×3 (15 mm)	45	18.0	35
2	*trans*- 8.0	150	2.0	5—6	0.25	2×3 (18 mm)	78	19.5	35
3	*cis*- 8.0	75	1.0	5—6	0.3	2×3 (15 mm)	72	21.6	35—40

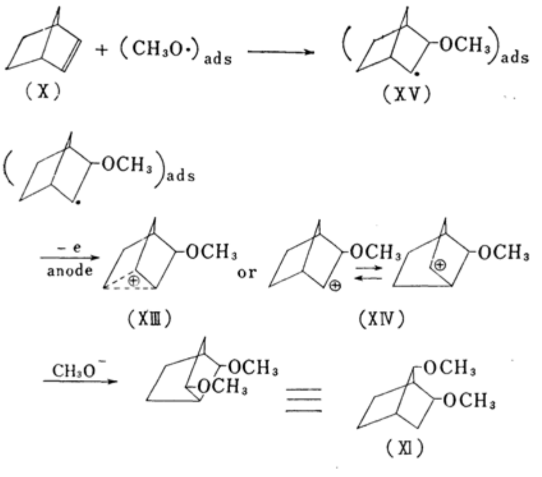
Expt. No.	Product  $C_6H_5CH(OCH_3)-CH(OCH_3)C_6H_5$ (*meso*-) g	%[a]	 $C_6H_5CH(OCH_3)-CH(OCH_3)C_6H_5$ (*dl*-) g	%	Liquid product g	%	$(C_6H_5CH_2)_2$ g	%	$(C_6H_5CH)_2$ g	%
1	1.0	20	2.2	44	0.7	14	trace		0.1	2
2	1.1	14	2.4	30	0.8	10	0.1	1.2	0.5	6.5
3	2.1	26.3	1.4	17.5	1.0	12.5	0.5	6.5	0.3	4

a) Based on the starting stilbenes.

TABLE 2. ELECTROLYSIS IN THE PRESENCE OF ELECTROLYTES

Stilbene g	Electrolyte g	Main product g	
trans- 5.0	CH_3ONa Na, 2.0	 $C_6H_5CH(OCH_3)-CH(OCH_3)C_6H_5$ *meso*- 1.0	 $C_6H_5CH(OCH_3)-CH(OCH_3)C_6H_5$ *dl*- 2.2
trans- 5.0	NH_4ClO_4, 5.1	C_6H_5CHO 2.5	
trans- 5.0	NH_4Br, 8.5	 $C_6H_5CHBr-CHBrC_6H_5$ *erythro*- 2.8	 $C_6H_5CHBr-CH(OCH_3)C_6H_5$ *erythro*- 1.4

* CH_3OH, 150 m*l*; electrode, Pt, 2×3 cm^2; volt, 5—6; current, 0.3—0.5 A; temperature, 35—40°C.



may be due to the methanolysis of a norbonyl cation (XIII or XIV) produced by the anodic oxidation of an intermediate radicals (XV).

Although it is still not clear whether the rearrangement of the norbornyl cation proceeds *via* a non-classical structure (XIII) or an equilibrium of classical structures (XIV), the fairly high yields and the stereospecificity of the products in this electrolysis indicate that the intermediate radical (XV) can easily be oxidized to the carbonium ion (XIII or XIV). No rearrangement product is known to arise from a radical addition to norbornene or in reactions of the norbonyl free radical.[14,15]

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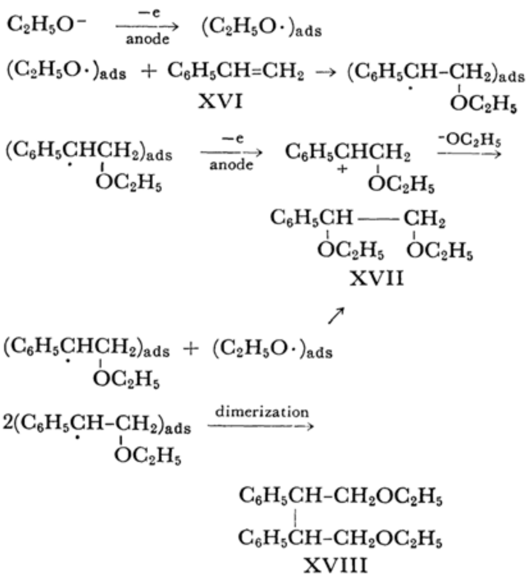
[14] S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 6309 (1957); **80**, 635 (1958).

[15] H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

Such rearrangements of carbonium ions in the anodic oxidation of *exo*- or *endo*-norbornane-2-carboxylic acid have been reported by Corey and his co-workers.⁴⁾

The Anodic Oxidation of Ethanol. When the electrolysis of ethanol containing sodium ethoxide was carried out in the presence of styrene (XVI), styrene glycol diethyl ether (XVII) was obtained in a 15% current yield, along with *meso*-1, 4-diethoxy-2, 3-diphenyl butane (XVIII) and a small amount of an unidentified liquid product. The gaseous products, methane, ethane and hydrogen, were detected by gas chromatographic analysis.

The formation of styrene glycol diethyl ether and 1, 4-diethoxy-2, 3-diphenyl butane may be represented by a scheme similar to that proposed above:



$$C_2H_5O^- \xrightarrow[\text{anode}]{-e} (C_2H_5O\cdot)_{ads}$$

$$(C_2H_5O\cdot)_{ads} + \underset{\text{XVI}}{C_6H_5CH{=}CH_2} \rightarrow (C_6H_5\dot{C}H\text{-}\underset{OC_2H_5}{CH_2})_{ads}$$

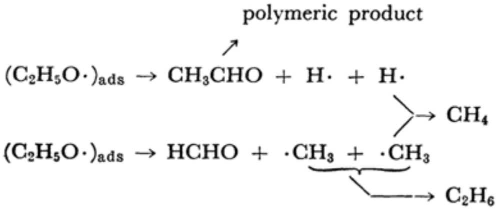
$$(C_6H_5\dot{C}H\underset{OC_2H_5}{CH_2})_{ads} \xrightarrow[\text{anode}]{-e} C_6H_5\overset{+}{C}H\underset{OC_2H_5}{CH_2} \xrightarrow{-OC_2H_5} \underset{\text{XVII}}{\underset{OC_2H_5}{C_6H_5CH}\text{——}\underset{OC_2H_5}{CH_2}}$$

$$(C_6H_5\dot{C}H\underset{OC_2H_5}{CH_2})_{ads} + (C_2H_5O\cdot)_{ads} \nearrow$$

$$2(C_6H_5\dot{C}H\text{-}\underset{OC_2H_5}{CH_2})_{ads} \xrightarrow{\text{dimerization}} \underset{\text{XVIII}}{\begin{array}{c} C_6H_5CH\text{-}CH_2OC_2H_5 \\ | \\ C_6H_5CH\text{-}CH_2OC_2H_5 \end{array}}$$

In addition to the products mentioned above, a polymeric product, which was assumed to be a condensation product of acetaldehyde, was obtained in a fairly large amount. It seems that the formation of the polymeric product may be due to the more facile decomposition of ethoxy radicals into acetaldehyde in comparison with decomposition of methoxy radicals.¹⁶⁾

The formation of the polymeric and gaseous products may proceed according to the scheme proposed by Allen¹⁷⁾:



$$(C_2H_5O\cdot)_{ads} \rightarrow CH_3CHO \overset{\nearrow \text{ polymeric product}}{} + H\cdot + H\cdot$$

$$(C_2H_5O\cdot)_{ads} \rightarrow HCHO + \underbrace{\cdot CH_3 + \cdot CH_3}_{\rightarrow C_2H_6} \quad (H\cdot + \cdot CH_3 \rightarrow CH_4)$$

However, we have little experimental evidence bearing on the validity of this mechanism.

These results suggest that diethoxy derivatives may be easily synthesized from arylated olefins and ethanol in fairly high yields *via* electrode processes.

Experimental

The melting points and boiling points are uncorrected. Electrolyses were carried out by using two platinum-foil electrodes with an apparatus previously described.¹⁾

Materials. *trans*-Stilbene¹⁸⁾ was recrystallized from ethanol to a constant mp (124.5—125°C). *cis*-Stilbene was obtained by the catalytic decomposition of α-phenyl-*trans*-cinnamic acids, which had been prepared by Buckles and Bremer's method¹⁹⁾; bp 120—123°C/2—3 mmHg, $n_D^{21}=1.6208$. Norbornene was prepared by Meinwald's method²⁰⁾ and purified by redistillation; bp 95—98°C, mp 44—45°C (in a sealed tube). Commercial styrene was carefully purified in the usual manner and distilled before use. Methanol was purified in a manner described earlier,¹⁾ while ethanol was purified by distillation in the presence of metallic sodium. These materials were confirmed to be pure by a study of their infrared spectrum and by gas chromatography.

The Anodic Oxidation of Methanol in the Presence of *trans*-Stilbene. Metallic sodium (2.0 g) was dissolved in 150 m*l* of methanol, and then 5.0 g of *trans*-stilbene was added to the solution. Dry nitrogen was bubbled through the mixture for 1 hr. Then, the mixture was electrolyzed at 35°C for 45 hr under a nitrogen atmosphere. The current was controlled at nearly 0.3 A (5—6 V). The electrolyzed solution was neutralized with a 10% hydrochloric acid solution (pH 6.8—7.0), and then the methanol and a small amount of formaldehyde were evaporated in a vacuum. The white crystals (0.9 g) which precipitated from the residue were identified as *meso*-hydrobenzoin dimethyl ether, mp 139—139.5°C, from ether; a mixed-melting-point determination with an authentic sample showed no depression.

Found: C, 79.51; H, 7.60%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

The infrared spectrum of this compound showed the characteristic absorption band at 1105 cm⁻¹ (C–O–C) and was identical with that of an authentic sample.

The filtrate was poured into water (100 m*l*) and extracted with ether. The extract was dried over magnesium sulfate, and the ether was evaporated. The oily residue was then distilled under reduced pressure to give the following fractions:

Fraction	bp	Weight, g
1	∼130°C/2—3 mmHg	0.1
2	130—145°C/2—3 mmHg	3.7
3	residue	1.0

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16) P. Gray and A. Williams, *Chem. Revs.*, **55**, 239 (1959).

17) M. J. Allen, "Organic Electrode Process," Reinhold Publish. Co., N. Y. (1958).

18) "Organic Syntheses," Coll. Vol. III, p. 786 (1956).

19) *Ibid.*, Coll. Vol. IV, p. 857 (1963).

20) *Ibid.*, Vol. 37, p. 65 (1957).

Fraction 2 was cooled below 0°C to give white crystals (1.6 g) of *dl*-hydrobenzoin dimethyl ether, mp 91—92°C, from methanol (lit., mp 92—93°C); a mixed-melting-point determination with an authentic sample showed no depression.

Found: C, 79.22; H, 7.29%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

The infrared spectrum of this compound showed the characteristic absorption band at 1090 cm^{-1} (C-O-C) and was identical with that of an authentic sample.

A mixture of fraction 1 and the filtrate (2.1 g) was chromatographed over active alumina (2.5×40 cm). Elution with benzene led to the isolation of the following products: *meso*-hydrobenzoin dimethyl ether (0.1 g), *dl*-hydrobenzoin dimethyl ether (0.6 g), unreacted stilbene (0.1 g), bibenzyl (a trace), and oily products (0.7 g).

Bibenzyl was identified by a mixed-melting-point determination with an authentic sample; mp 52—52.5°C.

Found: C, 92.09; H, 7.55%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

The infrared spectrum of the oily products showed the characteristic absorption band at 1115 cm^{-1}(C-O-C); by a comparis on of the spectrum with that of an authentic sample, the products were assumed to consist, mainly, of α-methoxy bibenzyl. The oily products were not further investigated.

Fraction 3 was chromatographed over active alumina (2.5×40 cm), but no products were detected upon elution with benzene.

The Anodic Oxidation of Methanol in the Presence of *cis*-Stilbene. Metallic sodium (1.0 g) was dissolved in 75 m*l* of methanol, and then 8.0 g of *cis*-stilbene was added to the solution. After dry nitrogen had been bubbled through the mixture, the mixture was electrolyzed at 35—40°C for 72 hr, with the current being maintained at nearly 0.3 A (5—6 V). The reaction mixture was then worked up in a manner similar to that used for *trans*-stilbene; *meso*-hydrobenzoin dimethyl ether (2.0 g) was obtained from the residue. From the ether extract, the following fractions were obtained:

Fractions	bp	Weight, g
1	125—135°C/3 mmHg	3.0
2	135—150°C/3 mmHg	2.3
3	residue	1.2

A mixture of fractions 1 and 2 was cooled below 0°C to give 1.0 g of *dl*-hydrobenzoin dimethyl ether. When the filtrate was chromatographed over active alumina (2.5×40 cm) and eluted with benzene, the following products were isolated: *meso*-hydrobenzoin dimethyl ether (0.1 g), *dl*-hydrobenzoin dimethyl ether (0.4 g), bibenzyl (0.5 g), unreacted stilbene (0.3 g), and oily products (1.0 g). Fraction 3 was chromatographed over active alumina, but, again, no products were detected.

The Electrolysis in the Presence of Ammonium Perchlorate. Ammonium perchlorate (5.1 g) and *trans*-stilbene (5.0 g) were dissolved in 150 m*l* of methanol, and then dry nitrogen was bubbled through the mixture. The mixture was electrolyzed at 34—40°C for 49 hr, with the current being maintained at nearly 0.3 A (5—6 V). When the electrolyzed solution was distilled, formaldehyde was obtained as its 2, 4-dinitrophenyl hydrazone (1.3 g) from the lower-boiling fraction. The residue was poured into water (100 m*l*), neutralized with a 10% hydrochloric acid solution, and extracted with ether. From the extract, the following fractions were obtained upon vacuum distillation:

Fraction	bp	Weight, g
1	40—55°C/4 mmHg	1.5
2	55—65°C/4 mmHg	0.7
3	65—110°C/4 mmHg	0.6
4	residue	3—3.5

By gas chromatographic analysis (column: Poly Ethylene Glycol, 6000, 3 m; carrier gas, H_2; temperature, 192°C), it was shown that fractions 1—3 were mixtures of benzaldehyde and a small amount of unidentified miscellaneous products, and that the total amount of benzaldehyde was 2.5 g.

Fractions 1 and 2 were left standing at room temperature for 2 or 3 days to give benzoic acid, mp 120°C, from water (lit., mp 120—121°C); a mixed-melting-point determination with an authentic sample showed no depression.

When fraction 3 was added to the 2, 4-dinitrophenyl hydrazine solution, it gave a 2, 4-dinitrophenyl hydrazone derivative, mp 92—93°C; a mixed-melting-point determination with an authentic sample of the 2, 4-dinitrophenyl hydrazone of benzaldehyde showed no depression. Fraction 4 was chromatographed over active alumina (2.5×25 cm), but no product was detected upon elution with benzene.

The Electrolysis in the Presence of Ammonium Bromide. Ammonium bromide (8.5 g) and *trans*-stilbene (5.0 g) was added to 150 m*l* of methanol and the mixture was electrolyzed at 30—41°C for 45 hr, the current being maintained at nearly 0.5—0.45 A (4—5 V). The solid product which precipitated during the electrolysis was filtered and then purified by recrystallization from benzene. This product was stilbene dibromide, mp 235—236°C (1.8 g); a mixed-melting-point determination with an authentic sample showed no depression.

Found: C, 49.92; H, 3.09%. Calcd for $C_{14}H_{12}Br_2$: C, 50.22; H, 3.39%.

The filtrate was poured into water to give a solid product (2.5 g). The solid was dissolved in benzene and was chromatographed over active alumina (2.5×50 cm). Elution with benzene led to the isolation of *meso*-hydrobenzoin dimethyl ether (0.3 g) and α-methoxy-β-bromo-1, 2-diphenyl ethane (1.4 g). These products were identified by mixed-melting-point determinations with authentic samples: α-methoxy-β-bromo-1, 2-diphenyl ethane, mp 115—116°C; and *meso*-hydrobenzoin dimethyl ether, mp 141—142°C.

The oily products obtained from the filtrate were neutralized with a 10% hydrochloric acid solution and extracted with ether. The extract was evaporated to give an oil (1.0 g). The oil was chromatographed over active alumina (2.5×40 cm; eluted with benzene) to isolate stilbene α-dibromide (0.2 g) and *meso*-hydrobenzoin dimethyl ether (0.1 g) from unidentified products.

The Anodic Oxidation of Methanol in the Presence of Norbornene. Metallic sodium (0.5 g) was dissolved in 80 g of methanol, and then norbornene

(14.1 g, 0.15 mol) was added to the solution. After dry nitrogen had been bubbled through, the mixture was electrolyzed at 8—12°C for 42 hr, with the current being maintained at nearly 0.5—0.6 A (20—30 V, 24.9·A·hr). The electrolyzed solution was then worked up in a manner similar to that described above; it gave the following fractions:

Fraction	bp	Weight, g
1	trapped	3.8
2	~75°C/30—32 mmHg	0.4
3	75—115°C/30—32 mmHg	4.2
4	~140°C/1.5 mmHg	2.0
5	residue	1.8

By gas chromatographic analysis (column, Silicon-550 and Poly Ethylene Glycol 6000, 3 m; carrier gas, H_2; temperature, 145°C), it was shown that fractions 2 and 3 were a mixture of unreacted norbornene, *exo-syn*-2, 7-dimethoxy bicyclo (2, 2, 1) heptane (1.7 g), two unidentified dimethoxy products (0.6 g and 0.5 g), and *exo*-2-methoxy bicyclo (2, 2, 1) heptane (1.0 g).

When fractions 2 and 3 were then submitted to preparative gas chromatography (column, P. E. G. 6000, 3 m; carrier gas, N_2; temperature, 132°C), four fractions were isolated.

Fraction a) was *exo-syn*-2, 7-dimethoxy bicyclo (2, 2, 1) heptane; bp 50—51°C/1.5 mmHg, $n_D^{26.5}=1.4600$.

Found: C, 69.32; H, 10.10%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

The infrared spectrum of this compound showed the characteristic absorption bands at 1110 and 1120 cm^{-1} (C–O–C), and the infrared spectrum, NMR and gas chromatographic analysis were identical with those of an authentic sample.

Fraction b), bp 90—92°C/20 mmHg, was assumed to be *trans*-2, 3-dimethoxy bicyclo(2, 2, 1) heptane on the basis of the infrared spectrum (1105 and 1120 cm^{-1} (C–O–C)) and NMR data, but the identity of this compound was not further established.

Fraction c) was *exo*-2-methoxy bicyclo(2, 2, 1) heptane, bp 63°C/30 mmHg, identified by a study of its infrared spectrum, by gas chromatographic analysis, and by a comparison of its spectrum with that of an authentic sample.

Fraction d) was a volatile product, the infrared spectrum of which showed no characteristic absorption bands of methoxy groups.

The Anodic Oxidation of Ethanol in the Presence of Styrene. Metallic sodium (1.0 g) was dissolved in 100 g of ethanol, and then 52 g of styrene was added to the solution. After dry nitrogen had been bubbled through, the mixture was electrolyzed at 35—40°C, 1.0—0.2 A (100—120 V) for 20 hr. During the electrolysis, a polymeric material was deposited on the electrode surface, and the current had decreased to 0.2 A (120 V) by the end of the electrolysis. The electrolyzed solution was filtered to give a polymeric product (4.5 g, washed with methanol). When the filtrate was worked up in a manner similar to the procedure described above, it gave the following fractions:

Fraction	bp	Weight, g
1	50— 57°C/25 mmHg	32.0
2	60— 95°C/0.3 mmHg	7.1
3	95—160°C/0.3 mmHg	2.3
4	residue	6.5

By gas chromatographic analysis (column, Silicon-550, 3 m; carrier gas, H_2; temperature, 172°C), it was shown that fraction 2 was a mixture of styrene glycol diethyl ether (6.5 g) and a small amount of miscellaneous products (0.3 g). When fraction 2 was distilled through a five-foot vacuum-jacketed column packed with glass helices, pure styrene glycol diethyl ether was isolated; bp 87.5—88°C/1.5 mmHg, $n_D^{18.5}=1.4840$.

Found: C, 73.85; H, 9.11%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

The infrared spectrum of this ether showed the characteristic absorption bands at 1110 cm^{-1}(C–O–C), and the NMR spectrum (with CCl_4 as the solvent) showed peaks at 2.97 (C_6H_5–), 5.82 (–CH–), 6.77 (–CH_2–), 8.91 and 8.87 τ (–CH_3); the peak areas were in the ratio of 5 : 1 : 6 (three –CH_2–): 6 (two –CH_3), as would be expected from the structure.

Fraction 3 was left standing at room temperature to give white crystals, mp 91—92.5°C, from methanol (0.8—0.9 g).

Found: C, 80.16; H, 8.87%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

The infrared spectrum of this compound showed the characteristic absorption bands at 1110 and 1128 cm^{-1} (C–O–C). This compound was assumed to be *meso*-1, 4-diethoxy-2, 3-diphenyl butane on the basis of the elementary analysis and studies of its infrared spectrum and the results previously reported.[3] A mixture of the filtrates from fractions 3 and 4 was chromatographed over silica gel (2×45 cm), eluted with benzene, to obtain 1.4 g of 1, 4-diethoxy-2, 3-diphenyl butane.

The Syntheses of Authentic Sample.—*meso*-Hydrobenzoin dimethyl ether, mp 139—141°C, was prepared by the *O*-methylation of *meso*-hydrobenzoin[21] with methyl iodide and silver oxide.[22] *dl*-Hydrobenzoin dimethyl ether, mp 91—92°C, was prepared by the *O*-methylation of *dl*-hydrobenzoin[23] with methyl iodide and silver oxide.[22] *erythro*-Stilbene dibromide, mp 235—236°C, was obtained by the bromination of *trans*-stilbene.[24] α-Methoxy-β-bromo-1, 2-diphenyl ethane, mp 115—116°C, was prepared by the bromination of *trans*-stilbene.[25] *exo-syn*-2, 7-Dimethoxy bicyclo (2, 2, 1) heptane, bp 101—102°C/30 mmHg, $n_D^{26.5}=1.4592$, was synthesized by the procedure of Alder.[26] *exo-cis*-2, 3-Dimethoxy bicyclo (2, 2, 1) heptane, bp 98—99°C/28—30 mmHg, was prepared by the *O*-methylation of *exo-cis*-bicyclo (2, 2, 1) heptane-2, 3-diol[27] with *n*-butyl lithium and dimethyl sulfate.[3]

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