*The Homolytic Methoxylation of Aromatic Compounds by the Anodic Oxidation of Methanol**

By Tadao INOUE, Kikuhiko KOYAMA and Shigeru TSUTSUMI

(Received April 11, 1964)

In a previous paper,[1] we have described how the anodic oxidation of methanol in the presence of alkylated aromatic hydrocarbons produces α-methoxy derivatives, which might be formed by the reaction of a methoxyl radical generated by the electrolysis of methanol as an intermediate.

The present study was undertaken to provide additional information about the anodic methoxylation of aromatic compounds. Thus, diphenylmethane, indan and tetralin, which are known as compounds with hydrogen atoms reactive towards autoxidation[2] or other free-radical reactions,[3] were chosen as the aromatic compounds.

* Reported at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

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

2) H. Hartmann and M. Seiberth, *Helv. Chim. Acta*, **15**, 1390 (1932); H. Hock and W. Svemihl, *Ber.*, **66**, 61 (1933).

3) G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960); K. Sima, Y. Shigemitsu and S. Tsutsumi, This Bulletin, **35**, 1728 (1962).

TABLE I. ANODIC METHOXYLATION OF TETRALIN

Expt. No.	CH_3OH g. (mol.)	Metallic sodium g.	Tetralin g. (mol.)	Current density amp./dm²	Amp. hr.	Product I, α-methoxytetralin g.	% c)	Current yield, % d)
1 a)	75(2.34)	0.5	40(0.30)	8.3	30.0	9.0	22	10
2 b)	75(2.34)	0.5	40(0.30)	6.5	18.8	5.6	14	10
3 a)	75(2.34)	0.5	45(0.34)	8.3	35.0	13.1	29.1	13

a) The electrolysis was carried out under following initial electrolytic conditions: current, 0.5 amp.; volt, 15 V.; temp., 12°C.
b) The electrodes, 2.3×3.3 cm², were used.
c) Based on tetralin used.
d) The current yields are based on the calculation that two moles of methanol should be oxidized to give a one-mole of the product I.

TABLE II. ANODIC METHOXYLATION OF INDAN

Expt. No.	CH_3OH g. (mol.)	Metallic sodium g.	Indan g. (mol.)	Current density amp./dm²	Amp. hr.	Product II, α-methoxyindan g.	%	Current yield, %
1 a)	75(2.34)	0:5	40(0.34)	8.3	30.0	6.4	15.1	8

TABLE III. ANODIC METHOXYLATION OF DIPHENYLMETHANE

Expt. No.	CH_3OH g. (mol.)	Metallic sodium g.	Diphenyl-methane g. (mol.)	Current density amp./dm²	Amp. hr.	Product III, α-methoxydiphenylmethane g.	Current yield, %
1 e)	75(2.34)	0.2	26.5(0.15)	1.6~4.2	6.7	0.9	3.6
2 f)	100(3.1)	0.5	50 (0.27)	3.3	17.6	1.8	2.9

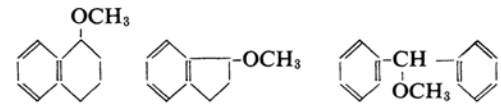
e) Initial electrolytic conditions: current, 0.1~0.25 amp.; volt, 7~12 V.; temp., 33°C.
f) Initial electrolytic conditions: current, 0.2 amp.; volt, 25 V.; temp., 33 °C.

Results and Discussion

The electrolyses were carried out using two platinum foil electrodes at 15~20°C, and the current density was kept approximately 8.3 amp./dm², according to the procedure described earlier.[1] The anodic oxidation of methanol containing sodium methoxide in the presence of tetralin afforded α-methoxytetralin (I) as a main product (current yield: 10~13%) and a small amount of formaldehyde, which was identified as its 2,4-dinitrophenylhydrazone, but the formation of the other isomeric methoxytetralin or of the dimeric product was not observed. When indan or diphenylmethane was used instead of tetralin, α-methoxyindan (II) (current yield: 8%) or α-methoxydiphenylmethane (III) (current yield: 2.9~3.6%) was obtained as the main product in each case. The experimental results obtained are summarized in Tables I, II and III. These products were analyzed by gas chromatography and infrared spectroscopy.

From these results, it can be considered that the methoxylated products are produced through a mechanism involving the attack of methoxy radicals upon the hydrocarbons; this hypothesis is based on the following reasons:

(A) The Position of Substitution: The reaction products clearly indicated that the methoxyl group was introduced in the α-position of the hydrocarbons, at which the hydrogen abstraction took place by ordinary free-radical reactions.[3-5]



(I) (II) (III)

(B) The Reactivity of the Aromatic Compounds: The relative reactivities were obtained by the following calculations: A/BC, where A: the yield (mol.) of α-methoxylated products; B: amp. hr. and C: the number of active hydrogen atoms.

TABLE IV. THE RELATIVE REACTIVITY OF THE AROMATIC HYDROCARBONS

Hydrocarbon	Product	A/B	A/BC
Diphenylmethane	III	6.7×10^{-4}	3.3×10^{-4}
Indan	II	14.4×10^{-4}	3.6×10^{-4}
Tetralin	I	23.1×10^{-4}	11.6×10^{-4}

The data given in Table IV indicate that the reactivity of these compounds in these electrolyses increases in the following order:

4) J. A. Meyer, V. Stannett and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 25 (1961).
5) G. A. Russell, ibid., **78**, 1047 (1956); A. L. Williams, F. A. Oberright and J. W. Brooks, ibid., **78**, 1190 (1956).

diphenylmethane < indan < tetralin

This increasing order of the reactivities of these hydrocarbons is also observed in other free-radical reactions involving ROO·, *t*-BuO· and CH_3· radicals.[4,5]

The results obtained here, however, show a remarkable contrast to the observations that a methoxyl radical formed by the decomposition of peroxides reacts with the aromatic hydrocarbons to give high yields of methanol and benzylic dimers, but no methoxylated products.[6,7] Such an anomalous reaction in these electrolyses can be explained as follows:

(a) Since the environment around the electrode might have a particularly high concentration of the methoxyl radical, the benzylic radicals resulting from the hydrogen abstraction by the methoxyl radical would be expected to react preferentially with the methoxyl radical and, consequently, not to give the dimeric products.

(b) As another possible rationalization, the following reaction path may be considered:

$$R\cdot \xrightarrow[\text{anode}]{-e} R^+ \xrightarrow{CH_3O^-} ROCH_3$$

Recently, Bonner and Mango[8] reported that electrolytically-generated benzyl radicals in the Kolbe electrolysis were oxidized with greater ease. Thus, the possibility that the free radical might be oxidized to carbonium ions to give solvolysis product can not be excluded in the present case.

Therefore, it may be assumed that the α-methoxylated products would be produced by the following course:

$$CH_3ONa \longrightarrow CH_3O^- + Na^+$$

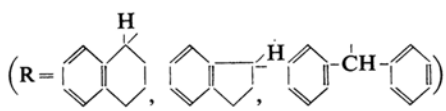
$$CH_3O^- \xrightarrow[\text{anode}]{-e} CH_3O\cdot$$

$$CH_3O\cdot + RH \longrightarrow CH_3OH + R\cdot$$

$$CH_3O\cdot + R\cdot \longrightarrow ROCH_3$$

or

$$R\cdot \xrightarrow[\text{anode}]{-e} R^+ \xrightarrow{CH_3O^-} ROCH_3$$



Experimental

All melting points and boiling points illustrated in the report are uncorrected. Electrolyses were carried out with the apparatus previously described.[1]

Materials.—When commercial tetralin was treated with solid sodium hydroxide and distilled from sodium, a fraction (b. p. 81.5~83°C/14 mmHg, $n_D^{20}=1.5380$) was collected. Indan was prepared by the reduction of α-chloroindan[9] with lithium aluminum hydride in a dry ethereal solution; b. p. 176~177°C (lit.,[10] b. p. 177°C), $n_D^{20}=1.5382$. Diphenylmethane was obtained commercially and was carefully distilled from sodium; b. p. 122~123°C/10 mmHg, $n_D^{20}=1.5767$. Methanol was purified in the manner described earlier.[1] These materials were confirmed to be pure by gas chromatography.

The Anodic Oxidation of Methanol in the Presence of Tetralin.—The reaction conditions and the yields of the product I are summarized in Table I.

R-3 is exemplified as follows: Metallic sodium (0.5 g., 0.022 mol.) was dissolved in 75 g. of absolute methanol, and then 45 g. of tetralin (0.34 mol.) was added to the mixture. After dry nitrogen had been bubbled through the mixture for about 1 hr., the mixture was electrolyzed at 12°C for 78 hr. and a current was maintained at nearly 0.5 amp. During the course of the electrolysis, tetralin was gradually dissolved and the electrolyzed solution turned brown in color. The reaction mixture was worked up in a manner similar to that used in an experiment described earlier.[1] After the ether had been removed, the oily residue (44.5 g.) was distilled under diminished pressure to give the following fractions:

Fraction	B. p., °C/mmHg	Weight, g.
1	40~62/1~2	29.3
2	62~83/1~2	8.3
3	83~120/1~2	1.6
4	Residue	2.0

By gas chromatographic analysis (conditions: column, P. E. G. 6000 and P. E. DA, 3 m.; column temperature, 160°C; carrier gas, H_2), it was shown that every fraction except fraction 4 was a mixture of unreacted tetralin and α-methoxytetralin, and that the total amount of this product was 13.1 g. Fraction 2 was chromatographed over silica gel (2.5×58 cm.). Elusion with benzene led to the isolation of unreacted tetralin, and α-methoxytetralin; b. p. 80~82°C/2 mmHg, $n_D^{15}=1.5363$.

Found: C, 81.22; H, 8.60. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

The infrared spectrum of the latter compound showed the characteristic absorption band at 1092 cm^{-1} (C-O-C of aliphatic ether) and was identical with that of an authentic sample prepared as described below.

The Synthesis of α-Methoxytetralin.—α-Methoxy-β-bromotetralin was prepared by the reaction of α, β-dibromotetralin with methanol according to the procedure of Braun;[11] b. p. 118~120°C/2~3 mmHg (lit., b. p. 151~152°C/13 mmHg). α-Methoxytetralin was prepared by the reduction of α-methoxy-β-bromotetralin with lithium aluminum hydride in dry ether and was purified by the column chromotography (column; silica gel, 2.5×58 cm.; eluted with

6) P. Gray and A. Williams, *Chem. Revs.*, **55**, 268 (1959).
7) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954).
8) W. A. Bonner and F. D. Mango, ibid., **29**, 430 (1964).
9) R. Weissgerber, *Ber.*, **44**, II, 1444 (1911).
10) A. V. Gross, J. M. Mavity and J. Mattox, *Ind. Eng. Chem.*, **38**, 1041 (1946).
11) J. V. Braun and G. Kirschbaum, *Ber.*, **54**, 612 (1921).

benzene). B. p. 80~81.5°C/1~2 mmHg, $n_D^{15}=1.5371$.

The Anodic Oxidation of Methanol in the Presence of Indan. — To a solution of sodium methoxide (0.5 g., 0.022 mol.) in 75 g. of absolute methanol, 45 g. (0.38 mol.) of indan was added. This new solution, after dry nitrogen had been bubbled through, was electrolyzed for 93 hr. under the following initial conditions: current, 0.5 amp.; volt, 15 V.; temperature, 12°C; current density, 8.3 amp./dm². During the course of the reaction, both electrodes were mutually exchanged at intervals to avoid the deposition of resinous materials. When the electrolyzed solution was treated in a manner similar to the experiment described earlier,[1] it gave the following fractions:

Fraction	B. p., °C/mmHg	Weight, g.
1	~50/1~2	24.5
2	50~82/1~2	7.9
3	82~100/1~2	3.0
4	Residue	3.5

Gas chromatographic analysis (column, P. E. G. 6000 and P. E. DA, 3 m.; column temperature, 159°C; carrier gas, H_2) showed that fractions 1, 2 and 3 were mixtures of unreacted indan and α-methoxyindan, and that the total amount of this product was 6.8 g.

Fraction 2 was chromatographed over silica gel and eluted with benzene to give following fractions:

Fraction	B. p., °C/mmHg	Weight, g.
a	55~57/10	1.5 $n_D^{20}=1.5380$
b	65~66/1~2	6.1 $n_D^{17}=1.5312$

Fraction a was identified as unreacted indan by gas chromatographic and infrared spectroscopic analysis.

Fraction b was identified as α-methoxylated indan, since the infrared spectrum of fraction b was identical with that of an authentic sample prepared by the following method and since it exhibited a characteristic absorption band at 1087 cm^{-1} (assigned to aliphatic ether C-O-C).

Found: C, 80.83; H, 8.39. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

The Synthesis of α-Methoxyindan.—α-Chloroindan was prepared by the reaction of indene with dry hydrochloric acid at 0~−10°C according to the procedure of Weissgerber.[9] B. p. 104~105°C/21~22 mmHg. α-Methoxyindan was prepared by the reaction of α-chloroindan with sodium methoxide in a methanol solution; b. p. 65~66°C/1~2 mmHg, $n_D^{17}=1.5312$.

The Anodic Oxidation of Methanol in the Presence of Diphenylmethane. —Metallic sodium (0.5 g.) was dissolved in 100 g. (3.1 mol.) of methanol, and then 50 g. (0.27 mol.) of diphenylmethane was added. The mixture was electrolyzed for 88 hr. under the following electrolytic conditions: current, 0.2 amp.; volt, 25 V.; temperature, 33°C; current density, 3.3 amp./dm². The reaction mixture was worked up in a manner similar to that used in an experiment described earlier.[1] From the ethereal layer, the following fractions were obtained:

Fraction	B. p., °C/mmHg	Weight, g.
1	102~111/2~3	39.3
2	111~126/2~3	2.5
3	126~152/2~3	1.1
4	Residue	4.5

By gas chromatographic analysis (conditions: column, P. E. G. 6000, 3 m.; column temperature, 192°C; carrier gas, H_2), it was also shown that every fraction except fraction 4 was a mixture of unreacted diphenylmethane and α-methoxydiphenylmethane, and that the total amount of this product was 1.8 g.

Fractions 2 and 3 were submitted to preparative gas chromatography (column, P. E. G. 6000, 6 m.; column temperature, 190°C; carrier gas, N_2), and the pure α-methoxydiphenylmethane was isolated; b. p. 120~121°C/2~3 mmHg, $n_D^{20}=1.5658$.

Found: C, 84.79; H, 7.19. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

The infrared spectrum of this product showed a strong C-O-C band at 1092 cm^{-1} and was identical with that of a sample prepared by the methylation of benzhydrol (0.015 mol.) with methyl iodide (0.09 mol.) and silver oxide (0.035 mol.); b. p. 120~121°C/2~3 mmHg, $n_D^{20}=1.5653$.

The authors wish to thank Dr. Yoshinobu Odaira and Dr. Noboru Sonoda for their helpful suggestions and encouragement.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka