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FREE RADICAL REACTIONS IN ORGANIC ELECTRODE PROCESSES—III*

THE REACTION OF AROMATIC HYDROCARBONS AT PLATINUM ANODE IN ACETONITRILE SOLUTIONS CONTAINING PERCHLORATE SUPPORTING ELECTROLYTES†

K. KOYAMA, T. SUSUKI‡ and S. TSUTSUMI
Department of Chemical Technology, Faculty of Engineering, Osaka University,
Miyakojima-ku, Osaka, Japan

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Abstract—The electrolysis of certain perchlorates in acetonitrile solutions has been carried out both in the absence and presence of aromatic hydrocarbons, such as toluene and cumene. The products formed indicate that the reactions involve oxidation of the hydrocarbons by perchlorate ions (or radicals). Oxygen-free coupling products of the hydrocarbons were detected, but the extent of these reactions is generally small. Possible reaction paths for the formation of these products are discussed.

ELECTROCHEMICAL processes involving the addition or removal of a single electron from an inorganic solute ion, may provide a convenient method for the generation of inorganic free radicals. Such electron transfer processes may be involved in anodic halogenations,[1] thiocyanation[2] and nitration,[3] which are carried out in the presence of organic compounds by the electrolysis of inorganic salts or acids in aqueous media.

Schmidt and Noack[4] reported that the electrolysis of perchlorates in acetonitrile leads to the quantitative generation of hydrogen ion at the anode, and to the formation of succinonitrile. They proposed that the anodic reaction proceeds through the discharge of a perchlorate anion to form the perchlorate radical i.e.:

$$ClO_4^- \rightarrow \cdot ClO_4 + e^-$$
$$MeCN + \cdot ClO_4 \rightarrow \cdot CH_2CN + H^+ + ClO_4^-$$
$$2\,\cdot CH_2CN \rightarrow NC{-}H_2C{-}CH_2{-}CN$$

Maki and Geske[5] observed an electron spin resonance spectrum of reactive intermediates generated by the electrolytic oxidation of acetonitrile solutions of lithium and sodium perchlorates shows a hyperfine structure of four equally spaced lines with approximately equal intensity, interpreted as due to the perchlorate radicals in support of the Schmidt-Noack sequence.

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* Part II, K. Koyama, K. Yoshida and S. Tsutsumi, *Bull. Chem. Soc. Japan* **39**, 516 (1966).

† Presented at *the 16th Annual Meeting of the Chemical Society of Japan*, Tokyo, April (1963).

‡ Present address: Basic Research Laboratories Toyo Rayon, Kamakura, Japan.

[1] M. J. Allen, *Organic Electrode Processes* p. 143. Reinhold, New York (1958).

[2] M. J. Allen, *Organic Electrode Processes* p. 161. Reinhold, New York (1958).

[3] K. Sugino, T. Shirai and T. Nonaka, *Abstracts of papers Presented at the 30th Annual Meeting of the Electrochemical Society of Japan* p. 115. Tokyo, Japan (1963).

[4] H. Schmidt and J. Noack, *Z. Anorg. u. Allgem. Chem.* **296**, 262 (1958).

[5] A. H. Maki and D. H. Geske, *J. Chem. Phys.* **30**, 1356 (1959).

Much attention[6,7] is still devoted to this anodic reaction at Pt electrodes, because of the growing interest in the use of acetonitrile as an electrochemical solvent, and the use of perchlorates as supporting electrolytes.

Based on these facts, perchlorate radicals, if formed at the anode, may attack an organic substrate present, giving rise to either hydrogen abstraction or the other reactions.[8]

RESULTS AND DISCUSSION

The electrolyses were carried out in an undivided cylindrical cell under a continuous stream of nitrogen. Parallel Pt sheets were usually employed as electrodes except for the experiment with silver perchlorate as an electrolyte, in which the electrolysis was carried out between a Pt anode and a Ag cathode.

Initial experiments were conducted in the absence of organic additives to investigate the electrochemical background reaction of an acetonitrile solution of lithium perchlorate. A small amount of current passed through the solution at the beginning of the electrolysis, rapidly dropped to near zero. Examination of the residual oil after removal of solvent and perchlorate from the electrolysed mixture indicated that succinonitrile is not formed in contrast to the result reported by Schmidt and Noack.[4]

In the experiments with added hydrocarbons, the current did not decrease so rapidly, and thus the electrolysis was continued until the current had been passed for the calculated period. The electrolysis of lithium perchlorate in acetonitrile in the presence of cumene yielded considerable amounts of 2-phenyl-2-propanol (I) together with traces of acetophenone (II) and a small quantity of 2,3-dimethyl-2,3-diphenylbutane (III). In addition to the above products, 4,4′-diisopropylbiphenyl (IV) was isolated from the experiment with ammonium perchlorate as electrolyte. The result obtained with a silver perchlorate electrolyte indicated the possible formation of 2 (isopropylphenyl) 2-phenylpropanes (V)—on the basis of b.p. and IR spectral comparisons with those reported previously.[9,10] In addition, a substance, m.p. 51°, which solidified on the wall of a cooler during vacuum distillation, was close to the m.p. (49°) of a compound produced together with IV by the action of Cu powder on *p*-iodocumene, and considered by Boedtker to be 2 (*p*-isopropylphenyl) 2-phenylpropane.[11] As has been pointed out,[9,10] isolation and characterization of each isomeric V is an arduous task.

When toluene was used as the organic additive, benzaldehyde (VI), 1,2-diphenylethane (VII) and 4,4′-dimethylbiphenyl (VIII) were produced. Although benzyl alcohol could not be detected, the IR bands at 3200–3350, 1285 and 1025 cm^{-1} suggest the formation of a OH compound.

All the products, except V, were identified by isolation and comparison with authentic samples.

The reaction conditions and the results are summarized in Tables 1 and 2, respectively.

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[6] J. P. Billon, *J. Electroanal. Chem.* **1**, 486 (1960).

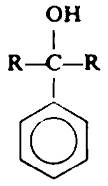
[7] J. P. Billon, *Bull. Soc. Chim. Fr.* 863 (1962).

[8] C. Walling, *Free Radicals in Solution* p. 31. Wiley, New York (1957).

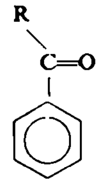
[9] P. Kovacic and A. K. Sparks, *J. Org. Chem.* **28**, 972 (1963).

[10] P. Kovacic and K. E. Davis, *J. Am. Chem. Soc.* **86**, 427 (1964).

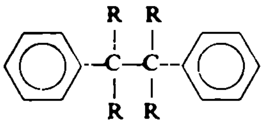
[11] E. Boedtker, *Bull. Soc. Chim. Fr.* **45**, 645 (1929); *Chem. Abstr.* **24**, 98 (1930).



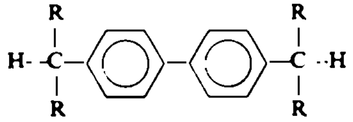
I: R = Me



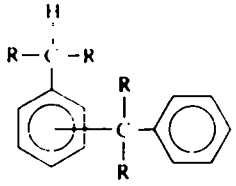
II: R = Me
VI: R = H



III: R = Me
VII: R = H



IV: R = Me
VIII: R = H



V: R = Me

The current applied for the identified products was based on the assumption that the following initial reaction occurs.

$$ClO_4^- + RH \rightarrow R\cdot + H^+ + ClO_4^- + e^-$$

TABLE 1. REACTION CONDITIONS[a,b] EMPLOYED FOR THE REACTION OF AROMATIC HYDROCARBONS AT Pt ANODES IN MeCN CONTAINING PERCHLORATE SUPPORTING ELECTROLYTES

Run No.	Electrolytes X^+	Electrolytes ClO_4^-	Aromatic[c] hydrocarbons	Electrodes[d] Anode	Electrodes[d] Cathode	Applied voltage	Temp	Total current
	X	mole				v		faraday
1	Li	0·01	cumene	Pt	Pt	5–10	3–5°	0·48
2	NH_4	0·01	cumene	Pt	Pt	5–10	2–5°	0·70
3	Ag	0·09	cumene	Pt*	Ag†	10–20	2–5°	1·15
4	Li	0·01	toluene	Pt	Pt	20–40	2–5°	0·78

[a] In each experiment, 200 ml of MeCN was used as solvent.

[b] Anode current density was maintained between 0·1 and 0·2 amp/dm².

[c] The amount of hydrocarbons used was 100 g.

[d] The electrodes used were 2 parallel plate electrodes, each measured 5 × 8 cm and spaced 5 mm apart.

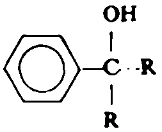
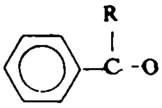
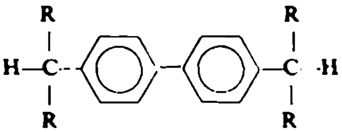
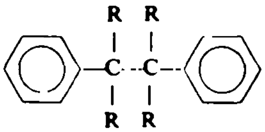
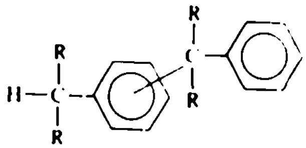
* cylindrical form

† It was measured 2·5 × 6 cm.

Results

(1) The main products identified in the experiments with added hydrocarbons were oxygenated compounds. Although there was evidence of oxidative coupling with the aromatic hydrocarbons, this generally was not significant. (2) Succinonitrile could not be detected nor did the IR spectra of mixtures display a band assignable to a cyano group, or VPC gives evidence of succinonitrile. (3) The presence of a chloride, probably hydrogen chloride, was obtained by precipitation as silver chloride by the passage of the gaseous products through aqueous silver nitrate solution. (4) The Pt anodes lost their metallic brightness during electrolysis, but no quantitative determination of this anode corrosion was made. (5) A change in the cation of the electrolytes had no significant effect on the variety of products and, therefore, these are formed at the anode.

TABLE 2. PRODUCTS OBTAINED FROM THE ANODE REACTION OF CUMENE AND TOLUENE

Run No.	Oxygenated products (g)		Oxidative coupling products (g)		
					
1 R = Me	4·0 (12)*	traces	—	0·05 (ca. 0·1)*	—
2 R = Me	1·2 (2·5)*	traces	0·1 (ca. 0·1)*	ca. 0·05	—
3 R = Me	0·5	traces	—	<0·05	<0·1
4 R = H	—	traces	0·03	<0·05	—

* Figures in parentheses are given for the current efficiency for the products.

The formation of oxygenated products must involve the oxidation of the hydrocarbons with oxygen (or air).[12] The source of the oxygen may be due to (1) traces of water in the solvent, (2) traces of oxygen dissolved in the solvent, or present in the electrolysis atmosphere, and/or (3) the oxygen liberated from perchlorate anions (or radicals) by degradation.

As the electrolyses were carried out in a nitrogen atmosphere, and dry acetonitrile was used as the solvent, it seems reasonable to assume that (3) is the most probable source of the oxygen. As mentioned, both the corrosion of Pt anodes and the generation of hydrogen chloride, are closely related to perchlorate degradation at the anode.

In support, evidence[13] was recently furnished that the anode background reaction of perchlorates in acetonitrile at Pt electrodes involves degradation of the perchlorates to lower oxidation states of chlorine, leading to an oxidative attack on the solvent. Although the detailed mechanism is not given, Russell also points out that the electron spin resonance spectrum observed[5] is probably due to chlorine dioxide rather than the perchlorate radical because the g-factor and coupling constant for the radical observed in the electrolysis agree with those for chlorine dioxide generated in the γ-irradiation of potassium perchlorate,[14] and the lifetime of the observed radical seems longer than one might expect for the perchlorate radical.

Based on these considerations, at least two reaction mechanisms are possible. The first involves the discharge of perchlorate anions leading to the generation of the perchlorate radicals as shown in Scheme I. The second, involves the generation of aromatic hydrocarbon cation radicals by loss of one π-electron from each hydrocarbon molecule followed by either their coupling or the reaction with perchlorates (Scheme II).

For both schemes, there are numerous additional reaction paths including oxidation with the chlorine compounds such as ClO_3^-, ClO_2, ClO_2^- and Cl_2O, and, thereby, a fraction of the perchlorate will be reduced to chloride. It may be assumed that the alkoxy radical (XI) would form as an active intermediate.[12] It is, however, difficult to consider that a chain reaction mechanism is involved because all the reactions in both schemes probably occur on the electrode surface where the chain carriers could be destroyed to give less reactive species.

Although there is no evidence in favour of either scheme, the second is preferred. Recent voltammetric studies of aromatic hydrocarbons in acetonitrile using a rotating or vibrating Pt electrode with perchlorates as supporting electrolytes, suggest that the anodic waves are due to the removal of π-electrons from these compounds with formation of their cation radicals. The polarographic half-wave oxidation potentials of benzene, toluene and xylenes recently reported[15] are 2·08, 1·98 and 1·56–1·58 v (*vs* a Ag–0·10N Ag^+ reference electrode), respectively and the discharge of the perchlorate anions occurs at an anode potential of 2·4 v (*vs* Ag–0·01M Ag^+).[7] These results suggest that the aromatic hydrocarbon ion radical is generated prior to the perchlorate radical.

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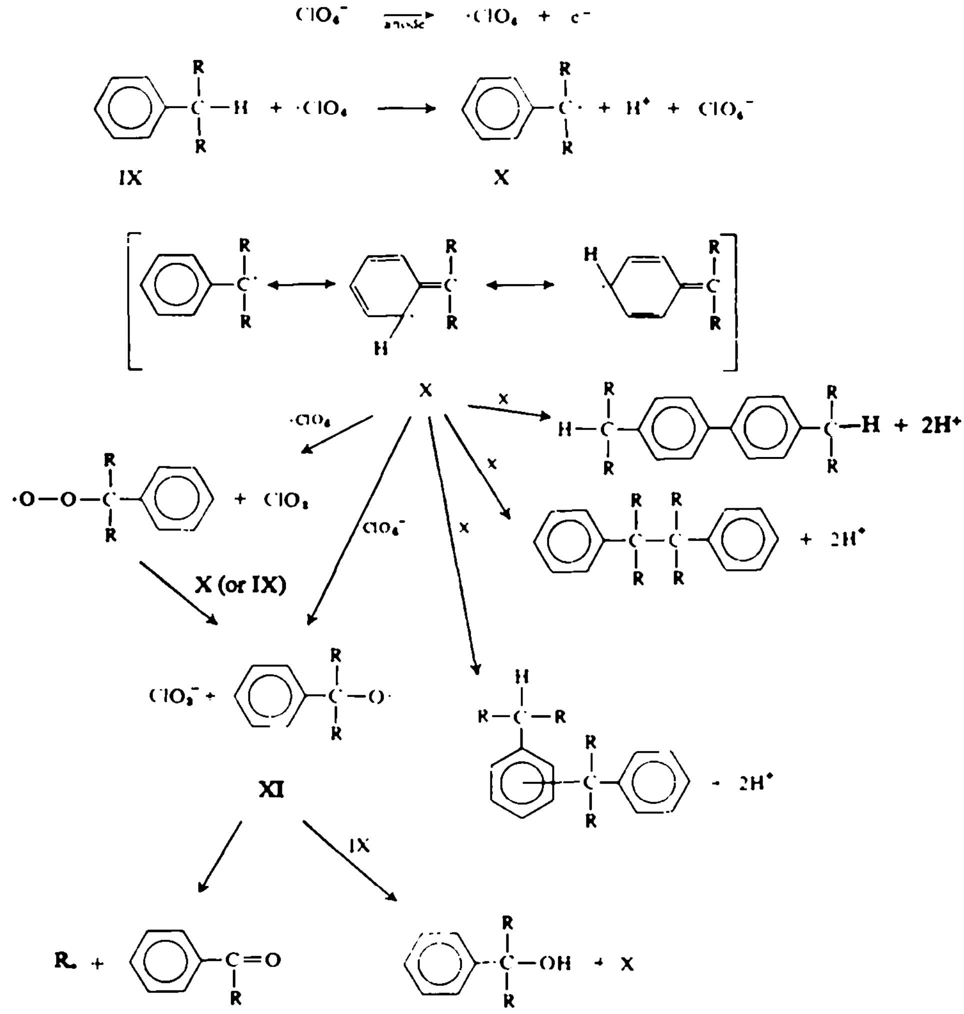
[12] C. Walling, *Free Radicals in Solution* p. 397. Wiley, New York (1957).

[13] C. D. Russell, *Analyt. Chem.* **35**, 1291 (1963).

[14] T. Cole, *Proc. Natl. Acad. Sci. U.S.* **46**, 506 (1960).

[15] W. C. Neikam and M. M. Desmond, *J. Am. Chem. Soc.* **86**, 4811 (1964).

SCHEME I



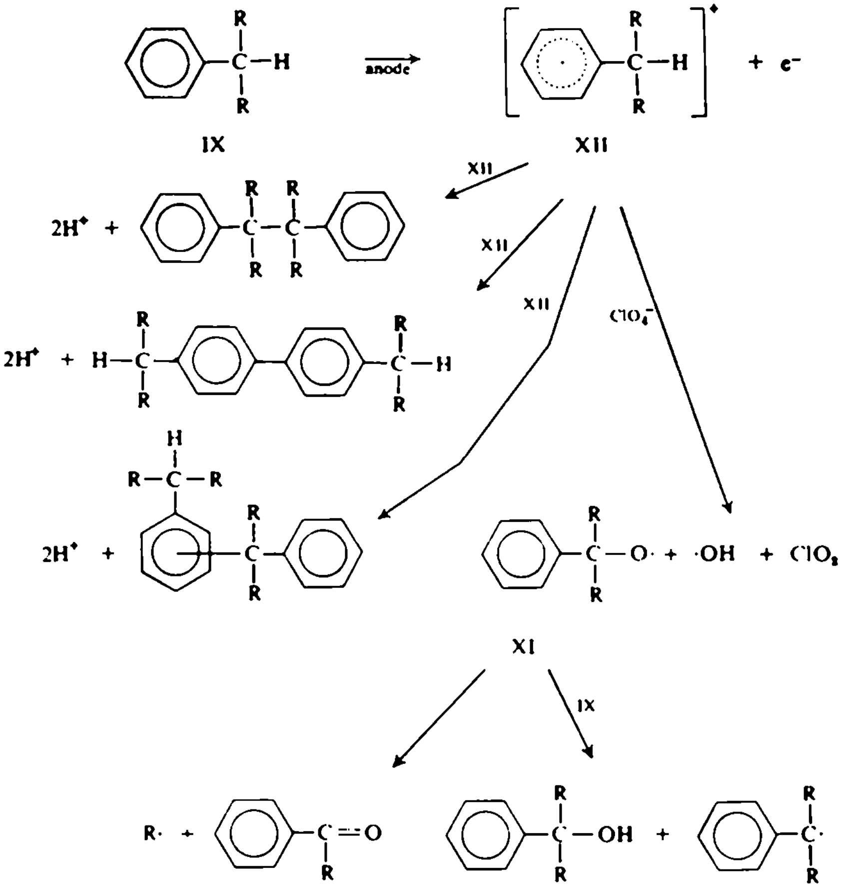
where R is Me or H.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra: Shimadzu IR spectrophotometer IR-27B; Shimadzu gas chromatograph GC-2A were employed for analysis of the products. The electrolyses were carried out in an undivided cylindrical cell fitted with a reflux condenser, N inlet tube and thermometer. The electrodes attached to glass tubes fitted through a rubber stopper were mounted in the center hole of the cell. The electrodes ordinarily used were 2 parallel Pt plates, each 5 × 8 cm and spaced 5 mm apart, except for the experiments with $AgClO_4$. The cell was cooled in a bath of cold water containing ice. The contents were stirred magnetically and N was passed through the soln during electrolysis. The N stream together with evolved gases was passed through $AgNO_3$aq placed in an washing bottle.

Materials. Commercially available MeCN was dried over anhyd $MgSO_4$, and then distilled from P_2O_5 through a Widmer column. The fraction b.p. 82° was collected for use as solvent. Toluene and cumene were obtained commercially, refluxed over Na, and then distilled through a 30 cm of column packed with metallic helices. The fractions b.p. 111° and 152–153°, were collected. Commercially

SCHEME II



where R is Me or H.

available $LiClO_4$ was dried at 150–160° under red. press. (20 mm) for 2 hr before use. $AgClO_4$ and NH_4ClO_4 were obtained commercially, dried under red. press., and used without further purification.

The electrolysis of acetonitrile solution of lithium perchlorate. The 2 Pt electrodes were each 2×3 cm, and 5 mm apart. A soln of $LiClO_4$ (2·2 g, 0·02 mole) in MeCN (150 ml) was electrolysed with an applied potential of 80–85 v at 5–10°. The initial small amount of current rapidly dropped to near zero, and, therefore, the total current passed was very small.

After removal of the perchlorate and solvent, distillation of the remaining oil (0·5 g) under red. press. (30 mm) gave no distillate.

Another run, using 0·5 g of the perchlorate as electrolyte under essentially identical conditions gave no indication (VPC) of the presence of succinonitrile.

The electrolysis of lithium perchlorate in the presence of cumene. A soln of $LiClO_4$ (1·0 g, 0·01 mole) and cumene (50 g, 0·42 mole) in MeCN (100 ml) was electrolysed at 3–5° with an applied potential of 5–10 v at a current density of ca. 0·1 amp/dm^2 until 0·24 faraday had been passed through the cell. At the end of the electrolysis, white ppts were observed in the $AgNO_3$aq.

The products obtained from 2 runs were combined, dissolved in ether (100 ml), washed 3 times with water (100 ml), dried ($MgSO_4$), and distilled, to yield after removal of the solvent, the following fractions: (A), wt. 7·0 g, b.p. −62° at 47 mm; (B), 57·8 g, b.p. 62–67° at 47 mm; (C), 1·0 g, b.p. 15–50° at 3 mm; (D), 6·7 g, b.p. 50–70° at 3 mm; (E), 10·0 g, b.p. 70–163° at 3 mm; (F), 12·3 g of black tarry residue. Fraction A gave a VPC displaying at least 3 peaks, and was found to consist mainly of unchanged cumene together with a trace of MeCN. Fraction B was the recovered cumene. Although these 2 fractions seemed to react with Br, no evidence for the presence of α-methylstyrene could be obtained. The IR spectra of fractions C and D (liquid films) exhibited the major absorption bands at 700, 765, 860, 910, 955, 1025, 1070, 1100, 1160, 1250, 1350–1370, 1440, 1490, 1590, 1655, 2910, 3000 and 3220–3300 cm^{-1}. The VPC analysis showed that fraction C consisted of unreacted cumene (traces) and I. The main peak on the VPC of fraction D was identical with that of I. These fractions, C and D, gave no observable peak having the same retention time as that of acetophenone. These VPC analyses were carried out by using a Silicone DC 550 column and H as carrier gas (0·45 kg/cm^2), at the column temp of 143°. Under these conditions, the retention times for cumene, I and II were 5·5, 8·0 and 15·5 min, respectively. Total yield of I based on the peak area on the VPC was 4·0 g.

The treatment of fraction D with α-naphthylisocyanate gave a white solid, m.p. 133–134°, which was identified as the α-naphthylurethane of I. The m.p. of this derivative was not depressed on admixture with an authentic sample and the IR spectra were identical. (Found: C, 78·45; H, 6·46. Calc. for $C_{20}H_{19}O_2N$: C, 78·66; H, 6·27%.)

Although *fractions* C *and* D *gave no peak corresponding to that of* II, (VPC), *the treatment of* D (1·09 g) with the freshly prepared 2,4-dinitrophenylhydrazine soln gave a trace amount (ca. 0·02 g) of a yellow ppt, m.p. 248–250°, characterized as 2,4-dinitrophenylhydrazone of II (lit[16] m.p. 250°) by the mixture m.p. test. The IR spectrum of this derivative agreed closely with that of an authentic sample.

A half portion (5·0 g) of fraction E was dissolved in EtOH, and water was added to the soln to precipitate on cooling a white solid (0·025 g), m.p. 114–118°, identified after recrystallization from EtOH-water as III, m.p. 119–120°, undepressed on admixture with an authentic sample. The IR spectrum of this crystal (KBr disk) was identical with that of the authentic sample, and displayed major absorption bands at 700, 730, 775, 915, 995, 1025, 1060, 1085, 1140, 1205, 1360, 1370, 1430, 1460, 1485, 1580 and 2900 c^{-1}. (Found: C, 90·50; H, 9·32. Calc. for $C_{18}H_{22}$: C, 90·70; H, 9·30%.)

Preparation of authentic 2-phenyl-2-propanol (I) *and its α-naphthylurethane*. A soln of MeMgI (from 12·2 g of Mg (0·5 g atom), 71 g (0·5 mole) of MeI and 200 ml of dry ether) was prepared in a 1-1. 3-necked flask equipped with a sealed mechanical stirrer, reflux condenser and a dropping funnel. To the stirred soln of MeMgI was added dropwise a soln of freshly distilled acetophenone (50 g, 0·4 mole) in dry ether (200 ml). After addition was complete, stirring was continued for 15 min, and then water was added to the soln. The ether was separated, dried over anhyd $MgSO_4$, and filtered. After evaporation of the solvent, the remaining oil was distilled under red. press. to yield crude I (42 g), b.p. 85–89° at 11 mm. Redistillation of I gave the authentic sample, b.p. 58–59° at 3 mm, n_D^{17} 1·5373, (Lit.$_D^{19}$ b.p. 94° at 13 mm, $n_D{}^{19}$ 1·5314).

Authentic α-naphthylurethane of I was prepared as described in the lit.[18] Preparation of authentic III was a modification of the method of Kharasch *et al.*[19] A soln of di-t-butyl peroxide (13·5 g, ca. 0·1 mole) in cumene (60 g, 0·5 mole) was introduced (over a period of 8 hr) beneath the surface of cumene (50 g, 0·42 mole) contained in a 300 ml 4-necked flask equipped with a reflux condenser, thermometer, dropping funnel and N inlet tube. The flask was immersed in an oil-bath held at 130–140°. During the heating, the N was allowed to flow over the surface of the soln. After the peroxide had completely been decomposed, evaporation of the unreacted cumene left a white solid (14 g). The recrystallization from EtOH-water gave III, m.p. 118–119° (Lit[19] m.p. 115°).

The electrolysis of acetonitrile solution of ammonium perchlorate in the presence of cumene. A soln of NH_4ClO_4 (1·0 g, 0·01 mole) and cumene (50 g, 0·42 mole) in MeCN (100 ml) was electrolysed at 2–5° with an applied potential of 5–10 v at a current density of 0·1–0·2 amp/dm^2. Total current passed was 0·35 faraday at the end of the electrolysis. The combined products of 2 experiments were dissolved

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[16] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds* p. 263. Wiley, New York (1948).

[17] I. Heilbron, A. H. Cook, H. M. Bunbury and D H. Hey, *Dictionary of Organic Compounds* (4th Edition) p. 2715. Eyre and Spottiswoode, London (1965).

[18] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds* (3rd Edition) p. 163. Wiley, New York (1948).

[19] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.* **10**, 401 (1945).

in ether, washed with water, dried over anhyd $MgSO_4$, and distilled, after removal of the solvent under diminished press, to yield the following fractions: (A), wt. 82 g, b.p. 37–115° at 12 mm; (B), 1·5 g, b.p. 20–80° at 3 mm; (C), 4·1 g, b.p. 80–130° at 3 mm; (D), 2·4 g, b.p. 130–135° at 3 mm; (E), 2·5 g of dark brownish solid residue. Fraction A consisted mainly of unchanged cumene. It reacted with Br, but no adduct was isolated. The IR spectrum of fraction B (liquid film) exhibited the absorption bands at 700(s), 763(s), 860(s), 910(w), 955(s), 995(w), 1025(m), 1070(m), 1100(m), 1173(s), 1250(m), 1365(s, broad), 1440(m), 1490(m), 1540(w), 1590(w), 1660(s), 2940(s) and 3350(s, broad) cm^{-1}, and was essentially identical with that of I except for the band at 1660 cm^{-1}. Fraction B was submitted to the VPC (columns: 25% Polyethylene glycol 6000 on Shimalite, and 25% Silicone DC 550 on Shimalite, each 3 m length; column-temp: 118°; carrier gas: H_2, 0·5 kg/cm^2), and was found to consist mainly of I (70% wt.), which had retention times of 25·5 for the former column and 23·5 min for the latter, respectively. A trace amount (ca. 3 mg) of 2,4-dinitrophenylhydrazone of II was obtained from 60 mg of fraction B.

The IR spectrum of fraction C (liquid film) was essentially identical with that of fraction B except for small differences in the relative intensity of bands at 862, 955 and 1295 cm^{-1}, and in the appearance of an additional band at 820(m) cm^{-1}. The VPC analysis of fraction C revealed the presence of at least 4 compounds, one of which was the carbinol I. The yield based on peak area on the VPC was 0·2 g.

Fraction D was triturated in an EtOH–water to yield white crystals (0·1 g), m.p. 63–65·5°. These were characterized after recrystallization from aqueous EtOH, as IV, m.p. 64–65° (Lit.[20]: m.p. 65–66°). The IR spectrum of IV (KBr disk) exhibited the absorption bands at 725(m), 820(s), 850(w), 890(w), 920(w), 1000(w), 1020(m), 1053(m), 1099(w), 1112(w), 1176(w), 1258(w), 1295(w), 1333(w), 1350(w), 1370(w), 1390(w), 1440(m), 1485(m) and 2875(m) cm^{-1}.

The VPC analysis (column, 25% Silicone DC 550 on Shimalite, 3 m length; column-temp, 180°; carrier gas, H_2, 0·95 kg/cm^2) of fraction D also indicated the presence of a component whose retention time (31 min) was identical with that of III, but the yield was very small (less than 0·05 g).

The electrolysis of acetonitrile solution of silver perchlorate in the presence of cumene. In this electrolysis, a cylindrical Pt plate anode (5 × 8 cm) was used, mounted around a Ag cathode (2·5 × 6 cm), and maintained 5 mm space between these electrodes.

To a soln of $AgClO_4$ (18 g, 0·09 mole) in MeCN (100 ml), cumene (50 g, 0·42 mole) was added. Electrolysis of the soln was carried out at 2–5° with an applied potential of 10–20 v at an anode current density of 0·2 amp/dm^2 until 0·58 faraday had been passed through the soln. The electrolysed solns obtained from 2 runs were combined, filtered to remove the metallic Ag deposited in the cell during electrolysis, and then worked as described in the experiment with $LiClO_4$ and cumene. Titration of acids present in the washing water with 0·5N NaOH indicated the formation of free acids (ca. 0·117 mole) probably in the forms of HCl and $HClO_4$. Distillation of the remaining oil gave the following fractions: (A), wt. 68 g, b.p. 45° at 20 mm; (B), 2 g, b.p. 35–50° at 3 mm; (C), 2·9 g, b.p. 50–135° at 3 mm; (D), 5 g of residue.

Fraction A was found to consist mainly of unreacted cumene. The VPC analysis of fraction B indicated the presence of a small quantity (less than 0·5 g) of I. Treatment of fraction B with an acidic 2,4-dinitrophenylhydrazine soln afforded trace amounts (2–3 mg) of the hydrazone of II. This hydrazone gave an IR spectrum identical with that of an authentic sample.

The IR spectrum of fraction C exhibited the absorption bands at 700(s), 758(s), 803(w), 940(w), 1030(m), 1055(w), 1075(w), 1105(w), 1203(w), 1275(w, broad), 1310(m), 1360–1380 (m, 3 bands), 1440(s), 1475(m), 1495(m), 1505(w), 1590(m), 1655(m), 1735(w), 1795(w), 1865(w), 1950(w), 2855(w, shoulder) and 2940(s) cm^{-1} which include all the bands assigned by Kovacic and Davis[10] to V with the striking similarity in the relative intensity. A portion (1 g) of fraction C was conducted to chromatographic purification to give slightly colored oil (0·1 g), b.p. 75–135° at 5 mm, which gave an IR spectrum displaying the absorption bands at 695(s), 755(s), 803(w), 828(w), 934(w), 1026(m), 1055(w), 1074(w), 1100(w), 1152(w), 1200(w), 1275(w), 1307(m), 1355(m), 1366(m), 1377(m), 1435(s), 1471(m), 1485(m), 1585(m), 1780(w), 1925(w), 2820(w), 2910(s), 2970(w) and 3003(w) cm^{-1}. The elemental analysis suggested that the oily material consisted of hydrocarbons.

A substance (ca. 0·1 g, m.p. 51–52°) solidified on the walls of a cooler during vacuum-distillation of fraction C. It was not further characterized, even though the m.p. was close to that (49°) of the compound characterized as 2-(*p*-isopropylphenyl) 2-phenylpropane.[11]

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[20] J. P. Morizur and R. Polland, *C.R. Acad. Sci. Paris* **254**, 1093 (1962).

A portion (0·35 g) of fraction C dissolved in EtOH, with the addition of water yielded a small amount of a slightly colored ppt. The IR spectrum (KBr disk) displayed the absorption bands at 697(s), 758(s), 803(w), 858(w), 913(w), 923(w), 936(w), 960(w), 1024(m), 1042(w), 1072(m), 1095(w), 1120(w), 1155(w), 1188–1198(w, 2 bands), 1272(w, 2 bands), 1305(m), 1356(m), 1375(m), 1430(m), 1445(w), 1470(m), 1488(m), 1580(w), 2815(w), 2900(m), 2950(w) and 2965(w) cm^{-1}. The structure of this substance was not determined.

The VPC analysis (column, 25% Silicone DC 550 on Shimalite, 3 m; column-temp, 175°; carrier gas, H_2, 1·0 kg/cm^2) indicated that fraction C also contained a small amount of III, whose retention time was 45 min.

The electrolysis of acetonitrile solution of lithium perchlorate in the presence of toluene. A soln of $LiClO_4$ (1 g, 0·01 mole) and toluene (50 g, 0·54 mole) in MeCN (100 ml) was electrolysed at 2–5° with an applied voltage of 20–40 v at a current density of ca. 0·1 amp/dm^2. The electrolysis was continued until 0·39 faraday had been passed through the soln. The electrolysed solns from 2 experiments were combined and worked up as described in the experiments with cumene. After removal of the solvent and unchanged toluene, the products were collected in 2 main fractions: (A), wt. 1·0 g, b.p.—21° at 10 mm; (B), 2·0 g, b.p. 21–110° at 10 mm; (C), 3·5 g, b.p. 110–153° at 10 mm; (D), 5·5 g of dark brownish tarry residue.

All fractions, especially fraction B, gave IR spectra displaying the absorption bands at 3200–3350(s, broad), 1285(s), 1025(s) and 1640–1650(vs, broad) cm^{-1}. These characteristic bands suggested the formation of oxygen-containing products, but benzyl alcohol could not be detected. The evidence for the formation of VI (traces) was obtained by treating fraction B with 2,4-dinitrophenylhydrazine soln. IR spectrum of this derivative was almost identical with that of an authentic sample.

The VPC (columns, 25% Polyethylene glycol 6000 on Shimalite and 25% Silicone DC 500 on Shimalite, each 3 m length; column-temp, 183°; carrier gas, H_2, 0·5 kg/cm^2) of fraction C revealed trace amounts of a compound with retention times (13·8 and 23·5 min for above 2 conditions, respectively) identical with those of the authentic VII.

The addition of water to a soln of fraction C in MeOH resulted in the precipitation of a solid (0·03 g), on cooling, which was characterized after recrystallization from MeOH–water as VIII, m.p. 121–122° (Lit.[21]: m.p. 121°). The IR spectrum (KBr disk) was identical in all respects with that appeared in the IR data[22] for VIII.

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[21] M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.* **48**, 1372 (1926).

[22] *IRD cards* (Edited by Infrared Data Committee of Japan) III, No. 1828 (1962).