Experimental Section

Materials. Palladium chloride, ammonium palladous chloride, rhodium trichloride, palladium bromide, iridium trichloride, platinum(II) potassium chloride, ruthenium trichloride, and platinum(IV) potassium chloride were purchased and used without purification. Alcohols and amines were purified by distillation. Aryl halides were purified by distillation or recrystallization.

An Example of Transfer Hydrogenolysis. Chlorobenzene (28 mg, 0.25 mmol), indoline (30 mg, 0.25 mmol), and $PdCl_2$ (5 mg, 0.028 mmol) were put into a Pyrex tube which had been sealed at one end, and the total volume of the solution was made 0.5 mL by the addition of methanol as a solvent. The tube was cooled with liquid nitrogen and sealed under vacuum. The sealed tube was heated for 4 h in a polyethylene glycol bath kept at 140 ± 1 °C. The reaction mixture was submitted to GLC analysis, which was performed at 90 °C using 2 m × 6 mm stainless steel column packed with 15% of Silicone DC-11 on Diasolid L and 30 μL of *n*-heptane as an internal standard. The amount of indoline and indole was measured by the use of a 2 m × 6 mm stainless steel column packed with 10% diethylene glycol succinate on Diasolid L and dibenzyl ether as an internal standard.

Other transfer hydrogenolyses were carried out in a similar way.

An Example of Kinetic Runs. Ten samples, prepared by the method described above, were heated at 70 ± 1 °C for 3, 6, 10, 15, 20, 30, 37, 45, 60, and 75 min. The reaction mixtures were submitted to GLC analysis.

References and Notes

(1) E. A. Braude, R. P. Linstead, K. R. H. Wooldridge, and P. W. D. Mitchell, *J. Chem. Soc.*, 3595 (1954); K. Kindler and K. Luhrs, *Justus Liebigs Ann. Chem.*, **685**, 36 (1965); *Chem. Ber.*, **99**, 227 (1966).

(2) Y. Sasson and G. L. Rempel, *Tetrahedron Lett.*, **36**, 3221 (1974); *Synthesis*, 448 (1975).

(3) F. R. S. Clark, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 121 (1975).

(4) R. Cramer and D. R. Coulson, *J. Org. Chem.*, **40**, 2267 (1975).

(5) P. Fitton and E. A. Rick, *J. Organomet. Chem.*, **28**, 287 (1971).

(6) A. J. Chalk and S. A. Magennis, *J. Org. Chem.*, **41**, 273 (1976).

(7) P. M. Maitlis "The Organic Chemistry of Palladium", Vol. I and II, Academic Press, New York and London, 1971.

(8) T. Nishiguchi, K. Tachi, and K. Fukuzumi, *J. Org. Chem.*, **40**, 240 (1975).

Anodic Oxidation of Cyclohexene in the Presence of Cyanide Ion

Kunihisa Yoshida,* Takahiro Kanbe, and Takayuki Fueno

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received October 18, 1976

The electrochemical oxidation of cyclohexene in methanol solution of sodium cyanide results in isocyanation as well as cyanation and methoxylation. The current efficiency of isocyanide increases outstandingly with increasing electrode potential. Current–potential data suggest adsorption of a product of the electrolysis on the electrode. The current efficiencies of products are dependent on the cyclohexene concentration, whereas the product distribution is found to be independent of the relative concentration of both electroactive species, i.e., CN^- and C_6H_{10}, on the electrode which changes with changing bulk concentration of cyclohexene. These observations indicate that a primary electron transfer from cyclohexene adsorbed while expelling an electrolysis product adsorbed is a key step to derive organic products.

Cyanation of olefins or dienes has been thus far unsuccessful. We previously reported on the products obtained from the electrochemical reaction of methanol solution of cyclohexene in the presence of mercuric cyanide and proposed simultaneous operation of both the substrate oxidation reaction and the ion discharge reaction to account for low yields of cyanated products.[1] Recently, however, several types of experimental evidence in favor of direct anodic oxidation of the substrate have been presented.[2-9]

Anodic oxidation of cyclohexene has received a great deal of recent attention.[10-23] Much of the interest in this compound has been due to the fact that it serves as an easily studied model for both addition and allylic substitution reactions to olefins. The present paper describes a careful study of the products of cyclohexene oxidation in the presence of cyanide. Some mechanistic experiments will also be reported and the formation of isocyanide will be discussed.

Results

Products. The electrolyses were conducted in methanol solution of sodium cyanide using a two-compartment cell under a nitrogen atmosphere in the potential region 1.9–2.7 V vs. SCE at platinum electrode. The products formed were identified as such from comparisons with the authentic samples prepared by other routes, and determined by VPC. Isolation of the various products was performed using preparative VPC techniques. Besides 3-methoxycyclohexene (**1**) and dimethoxymethylcyclopentane (**2**), 3-isocyanocyclohexene (**3**), 2-cyclohexene-1-carbonitrile (**4**), isocyanocyclohexane (**5**), cyclohexanecarbonitrile (**6**), and *trans*-2-methoxycyclohexanecarbonitrile (**7**) were found together with bis-2-cyclohexen-1-yl (**8**) and unidentified minor components. Traces of methoxycyclohexane and *trans*-1,2-dimethoxycyclohexane were also noted.

Current–Potential Data. Figure 1 presents current–potential curves for oxidation of sodium cyanide in methanol and for the same solution with added cyclohexene. As can be seen in Figure 1, a methanolic solution of sodium cyanide is discharged at about 1.5 V,[4] whereas the addition of cyclohexene results in a remarkable decreasing of the current in the region of 1.6–1.9 V. Under experimental conditions cyclohexene begins to be oxidized at about 2.0 V ($E_{1/2}$ = 1.89, 2.05, and 2.16 V vs. Ag,Ag$^+$,[10,17,24] 2.14 and 2.35 V vs. SCE[16,20]).

Cyclic voltammograms were taken at a platinum electrode in a solution of 0.1 M tetraethylammonium fluoroborate within the range of 1.0–2.2 V vs. SCE at 0.1 V/s. The background current is not affected by added sodium cyanide (concentration $\sim 10^{-2}$ M). With cyclohexene added (concentration $\sim 10^{-2}$ M) the current decreases instantaneously at essentially the same potential and the curve of current vs. potential falls below that for the system without the substrate. The trend does not change even when the order of addition of the substrate and the cyanide is inverted. This suggests that a product of the electrolysis would be adsorbed on the anode, thus decreasing the area available for the normal electrochemical reaction.

Influence of the Concentration. Table I summarizes the results of controlled potential electrolyses performed with

Table I. Anodic Oxidation of Cyclohexene in Methanolic Sodium Cyanide Solution[a]

[Cyclohexene], M	Oxidation potential, V vs. SCE	Anode material	Electricity, Faradays	n Faradays/mol	Current efficiency and yield,[d] %								
					1	2	3	4	5	6	7	8	3/4
0.08	2.0	Pt	0.011	9.7	5.9 (28.6)	2.5 (12.1)	0.40 (1.94)	0.21 (1.02)	0.02 (0.10)	0.02 (0.10)	0.02 (0.10)	0.01 (0.10)	1.9
0.40	2.1	Pt	0.030	5.3	13.6 (36.0)	5.0 (13.3)	0.74 (1.96)	0.39 (1.03)	0.08 (0.21)	0.06 (0.16)	0.02 (0.05)	0.04 (0.21)	1.9
0.80	2.1	Pt	0.030	3.9	24.0 (46.8)	9.6 (18.7)	1.09 (2.13)	0.64 (1.25)	0.08 (0.16)	0.07 (0.14)	0.05 (0.10)	0.21 (0.82)	1.7
1.60	2.1	Pt	0.020	2.4	20.0 (24.0)	7.0 (8.4)	1.30 (1.56)	0.68 (0.82)	0.13 (0.16)	0.09 (0.11)	0.07 (0.08)	0.75 (1.80)	1.9
2.40	2.1	Pt	0.015	1.7	19.6 (16.7)	6.4 (5.4)	1.72 (1.46)	0.75 (0.64)	0.15 (0.13)	0.10 (0.09)	0.09 (0.08)	2.12 (3.60)	2.3
0.80	2.4	Pt	0.035	3.7	25.1 (46.4)	9.9 (18.3)	2.50 (4.63)	0.74 (1.37)	0.27 (0.50)	0.11 (0.20)	0.10 (0.19)	0.14 (0.52)	3.4
0.80	2.7	Pt	0.025	3.2	24.4 (39.0)	10.3 (16.5)	3.83 (6.13)	0.82 (1.31)	0.43 (0.69)	0.23 (0.37)	0.10 (0.16)	0.17 (0.54)	4.7
0.80	2.1	C	0.014	3.2	21.5 (34.4)	7.2 (11.5)	0.94 (1.50)	0.51 (0.82)	0.05 (0.08)	0.06 (0.10)	trace	0.09 (0.29)	1.8
0.80[b]	2.0	Pt	0.037	1.8	57.5 (51.8)	26.7 (24.0)							
0.80[c]	1.4	Pt	0.028	13.8	0.6 (4.1)	0.1 (0.7)							

[a] [NaCN] = 0.80 M; temperature, 25 °C. Minor products: methoxycyclohexane, *trans*-1,2-dimethoxycyclohexane. [b] Methanolic sodium perchlorate solution (0.80 M). [c] Methanolic sodium methoxide solution (0.80 M). [d] The value in parentheses represents the chemical yield based on unrecovered cyclohexene.

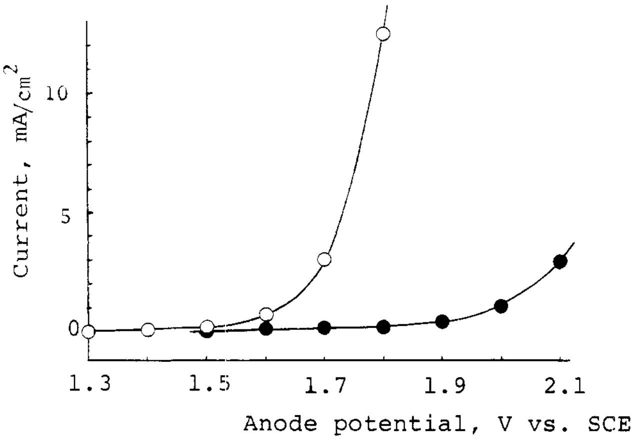


Figure 1. Plots of current vs. anode potential for electrolyses of solutions containing 0.8 M sodium cyanide in methanol at smooth platinum (8 cm^2) at 25 °C (solution magnetically stirred): ○, without cyclohexene; ●, with 0.8 M cyclohexene.

various initial concentrations of cyclohexene. Each current efficiency represents an average of three or more experiments conducted at the same potential.

The data listed in Table I clearly show that the current efficiency of products increased with increasing concentration of the substrate used; especially the current efficiency of formation of **8** is increased conspicuously. The chemical yield of products (based on unrecovered cyclohexene) increased with increasing cyclohexene concentration. Coulombic n value increases with decreasing cyclohexene concentration, whereas the product distribution is relatively constant with cyclohexene concentration from 2.40 M decreasing to 0.08 M (except for **8**, whose formation is second order in cyclohexene). Hence cyanide ion discharges concurrently at the lower concentration of cyclohexene probably to produce cyano radical, which does not enter into organic products but would attack the coexisting cyanide ion to form cyanogen anion radical[5] or dimerize to cyanogen.[25] The current efficiency for the reaction at the lower concentration of cyclohexene was 10% or so and the remainder of the current would be consumed with these inorganic electrode processes.

Influence of the Anode Potential. Comparative experiments were also carried out at different anode potential. The initial concentrations of sodium cyanide and cyclohexene were both fixed at 0.80 M. It is seen from Table I that the current efficiency of each product again increased with increasing potential. This observation taken together with the influence of bulk concentration of cyclohexene supports adsorption of the substrate on the electrode.[8,26] The current efficiency for the production of isocyanide increased outstandingly.

Influence of the Anode Materials and the Solvent. The electrooxidations were carried out at carbon and gold anodes in methanolic sodium cyanide solution to compare the role of anode materials. The current efficiencies for the production of the products are as shown in Table I. It is seen that at a carbon anode all the products are formed in almost the same current efficiencies as at a platinum anode. At gold, the electrode itself began to dissolve in the solution with the passage of a current. A trace amount of isocyanide **3** was detected, along with the methoxylated products (**1** and **2**).

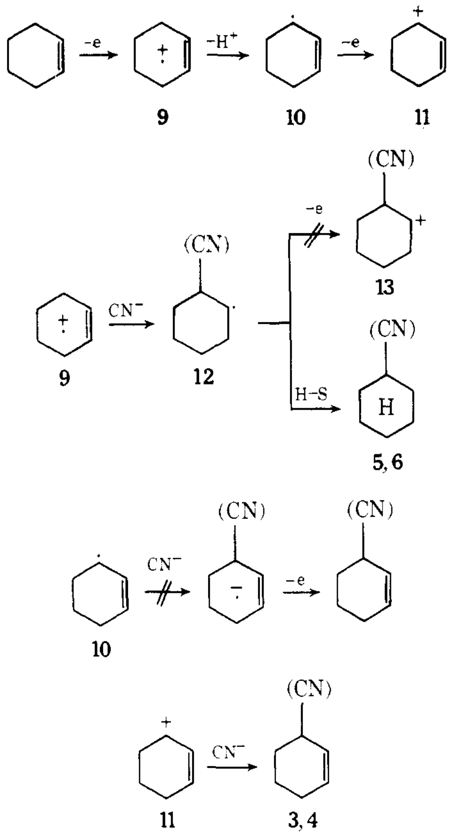
To study the influence of solvent, the anodic oxidation of cyclohexene was performed in acetonitrile containing tetraethylammonium cyanide. Neither cyanation nor isocyanation was observed, but a significant amount of tarry products was obtained.

Discussion

The observed products are formally a 2-equiv change. A mechanism involving direct anodic oxidation of the substrate is reasonable to account for the electrochemical behavior of cyclohexene and the relation between products and the cyclohexene concentration. Some of the current is consumed via electron transfer from the cyanide ion and this process does not produce isolable cyanated products.

According to the proposed mechanism in Scheme I, three types of intermediates are conceivable: cyclohexene cation radical **9** produced by an initial one-electron oxidation, 3-cyclohexenyl radical **10** produced by deprotonation of initially

Scheme I

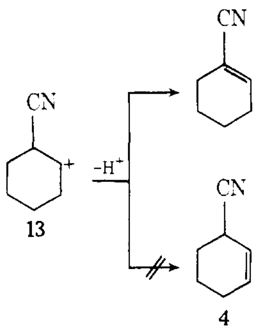


generated cation radicals, and 3-cyclohexenyl cation **11** formed by further anodic oxidation.

The anodically generated cation radical **9** is attacked by the cyanide ion to produce the radical **12**, followed by hydrogen atom abstraction from cyclohexene or the solvent methanol. Ionization energy of cyclohexene is moderately low[27–32] and the cyclohexene cation radical **9** has clearly been recognized in the gas phase.[33,34] Intervention of **9** has also been proposed to account for the products obtained from the oxidation reaction by means of cobaltic acetate[35] as well as anodic process.[17,20]

The radical **12** could be oxidized to the cation **13**, followed by proton release, thus leading to the allylic substitution products.[1,20] This possibility is ruled out from the fact that the solvolysis of *trans*-2-cyanocyclohexyl tosylate in methanolic cyanide solution produces 1-cyclohexene-1-carbonitrile at 25 °C exclusively. Under these conditions, the rate of isomerization of 2-cyclohexene-1-carbonitrile (**4**) to 1-cyclohexene-1-carbonitrile is extremely slow. The conjugated isomer was not detected in the electrochemical experiment. Anodically generated 2-methylcyclohexyl cation produces 1-methylcyclohexene.[36]

Scheme II



Neutral radicals can couple with nucleophiles such as cyanide ion.[37] 3-Cyclohexenyl radical **10** was generated from cyclohexene by irradiation of a solution containing di-*tert*-butyl peroxide and sodium cyanide. In this case, the allylic hydrogen abstraction is effected by *tert*-butoxy radicals from the photodissociation of the peroxide. A Pyrex filter was used in all experiments to ensure that direct excitation of alkene and/or adduct did not occur.[38–41] Bis-2-cyclohexen-1-yl (**8**) was formed effectively, whereas no cyanated or isocyanated product was observed.

Table II. Product Ratio in Allylic Substitution of Various Reactions

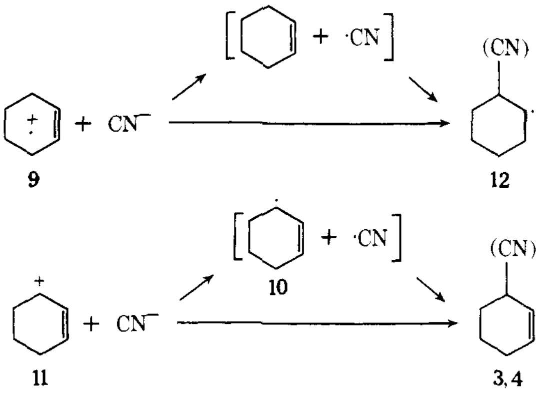
Reaction	3/4	1/4
Cyclohexene–NaCN–CH$_3$OH, 2.7 V	4.7	30
3-Bromocyclohexene–NaCN–CH$_3$OH, reflux	0.4	40
3-Bromocyclohexene–AgCN, room temp	9.2	

The reaction of the various cations with the cyanide nucleophile has been studied extensively.[42–44] 3-Cyclohexenyl cation **11** combines with cyanide ion to form the isocyanide **3** or the cyanide **4**. For comparison, the reaction of 3-bromocyclohexene with metallic cyanides was examined. The results are shown in Table II, together with the result of a potentiostatic experiment conducted at a higher potential. With sodium cyanide in methanol, cyanation surpassed isocyanation. On the contrary, with silver cyanide, isocyanation was brought about predominantly. Of interest are the results obtained with increased anode potential. The data listed in Table I clearly show that the relative ratio of two products (**3** and **4**) significantly increases as the electrode potential is made positive. The predominance of isocyanation in the present anodic reaction performed at relatively high electrode potentials would be ascribable to the interaction of cyanide ion with electrode surface (with a covalent bond character such as that in silver cyanide) and the different reactivity of anodically excited species.

In the anodic addition[4,6,8,9] or the substitution[7,43,45–48] involving aromatic cation radical intermediates, the carbon atom of cyanide ion acts as the nucleophilic center. A few reports have mentioned the coexistence of isocyanide in the reaction mixture from IR data.[49–51] The hard–soft acids–bases (HSAB) principle has been used with considerable success in rationalizing the reactivity pattern of ambident anions.[52–54] From the general experience the carbon nucleophiles are soft, as are carbanions, and nitrogen nucleophiles are hard, although the hardness is less pronounced when the nucleophilic nitrogen atom is part of a polarizable aromatic system as in pyridine. One may consider the carbon end the softer end, and the nitrogen end the harder end of the cyanide ion. In addition, cyclohexene cation radical **9** as well as π-3-cyclohexenyl cation **11** in question is harder than are the aromatic cation radicals concerned in cyanation, in which positive charge spreads over the whole molecule.

Scheme III is an attempt to describe the anodically gener-

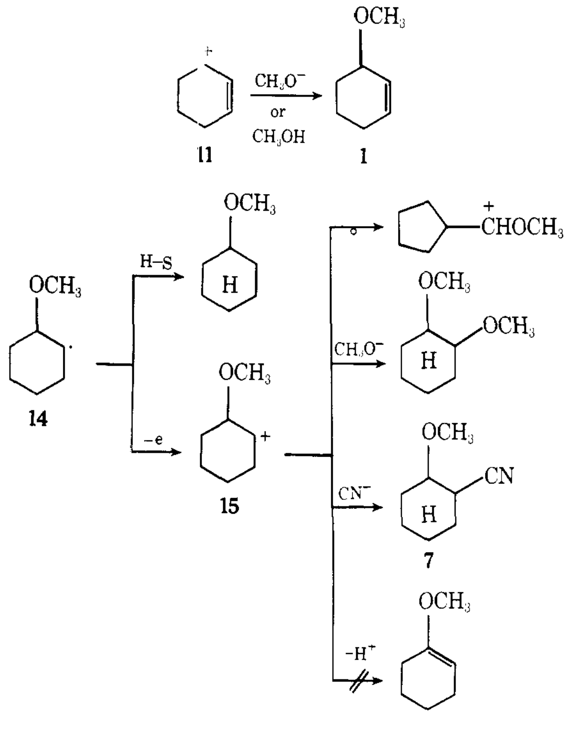
Scheme III



ated cationic species–cyanide anion combination reaction in more detail. The cationic species, **9** and **11**, would combine with cyanide anion directly or via an electron-transfer process.[55] In practice, a stable cation radical such as tri-*p*-anisylamine can oxidize cyanide ion to cyano radical,[7,25] whereas cyano radical can couple with cyclohexene or 3-cyclohexenyl radical **10**.[56] The reaction of perylene perchlorate with cyanide ion may be via the electron-transfer reaction in view of the stability of the former compound.[57] The cation radical–nucleophile combination reaction has attracted continuous attention.[58,59]

As in the cyanation and isocyanation reactions, methoxylation would proceed via the substrate discharge mechanism. There are some mechanistic works concerning the anodic methoxylation of cyclohexene[15,20] and consequently, an attempt was made to avoid repetition. The cation **11** combines with methoxide ion or the solvent methanol. Since an ionization potential of 2-methoxycyclohexyl radical **14** is lower than that of 2-cyanocyclohexyl radical **12**, the former radical would mainly be oxidized to the cation **15**, followed by a rearrangement of the carbon skeleton.[14,15,20,60] *trans*-2-Methoxycyclohexanecarbonitrile must come from the combination of the cation **15** and cyanide ion, because the foregoing solvolysis of *trans*-2-cyanocyclohexyl tosylate did not yield the cyanomethoxylation product. Unfortunately, the reaction between the cation **15** and cyanide ion could not be observed directly, since *trans*-2-methoxycyclohexyl tosylate did not undergo solvolysis in methanolic sodium cyanide solution.

Scheme IV



The product **8** arises from the dimerization of the radical **10**. This reaction competes with that of cationic species, **9** and **11**, with the electrolyte or the solvent. The second-order reaction is affected to a greater extent by an increase in the cyclohexene concentration on the electrode; thus a relatively high current efficiency for the formation of **8** is favored by the use of a concentrated solution of cyclohexene and a higher anode potential.

In conclusion, the anodic oxidation of cyclohexene in methanolic cyanide solution results in isocyanation as well as cyanation and methoxylation. Isocyanation is highly potential dependent. Current–potential data show that a product of the electrolysis is adsorbed on the anode. The substrate discharge mechanism can account well for the electrochemical behavior of cyclohexene and the observed products.

Experimental Section

Controlled potential electrolyses were performed by using a divided cell with a platinum wire electrode in the cathode compartment and the saturated calomel reference electrode, a platinum plate electrode having an area of 8 cm^2, and a magnetic stirrer bar in the anode compartment. Anode potential was controlled by means of a Yanaco Model VE-3 controlled potential electrolyzer.

Coulometry was carried out with a Hokuto Denko Model HF 108A current integrator.

Cyclic voltammetry was performed in a two-compartment cell in which the calomel reference electrode with an agar bridge was separated from the platinum anode and the cathode by a glass frit. The working electrode was a 1-cm platinum wire. A Hokuto Denko HB-107A voltage scanner, HA-104 potentiostat, and Yokogawa Type 3083 XY recorder were used. All measurements were carried out at 25 °C.

Materials. Methanol was purified by fractional distillation from magnesium methoxide. Reagent grade sodium cyanide was used with no purification other than drying. Tetraethylammonium cyanide was prepared according to the method given by Andreades and Zahnow.[5] Cyclohexene was prepared from cyclohexanol by dehydration with concentrated sulfuric acid[61] and was purified by distillation over sodium. *trans*-2-Methoxycyclohexyl tosylate was obtained from the standard procedure.[62] *trans*-2-Cyanocyclohexyl tosylate was also prepared from *trans*-2-hydroxycyclohexanecarbonitrile[63,64] and recrystallized from petroleum ether, mp 50–54 °C.

The following reference materials were prepared according to the literature: methoxycyclohexane,[65] 1-methoxycyclohexene,[66] cyclopentanecarboxyaldehyde,[67] cyclohexanemethanol,[68] dimethoxymethylcyclopentane,[69] cyclohexanecarbonitrile,[70] 1-cyclohexene-1-carbonitrile,[71] and isocyanocyclohexane.[72]

3-Methoxycyclohexene was obtained from 3-bromocyclohexene[73] by a modification of the method of Vogel,[65] bp 46 °C (27 mm) (lit.[14] bp 139–141 °C).

cis- and *trans*-1,2-dimethoxycyclohexane were prepared from the corresponding 1,2-diol[74,75] by the procedure of Hanze, Conger, Wise, and Weisbalt.[76]

2-Cyclohexene-1-carbonitrile was obtained by the reaction of 3-bromocyclohexene and potassium cyanide in acetone–water by the method of Mousseron, Winternitz, Jullien, and Jacquier.[77] The nitrile was obtained together with cyclohex-2-enol[78,79] and 3-isocyanocyclohexene (product ratio 7:11:1).

3-Isocyanocyclohexene was prepared by the reaction of 3-bromocyclohexene and silver cyanide according to a modification of the method of Jackson and McKusick.[80] Relative ratio of 3-isocyanocyclohexene and 2-cyclohexene-1-carbonitrile was 9:1. This isocyanide has not been reported previously.

trans-2-Methoxycyclohexanecarbonitrile was prepared from *trans*-2-hydroxycyclohexanecarbonitrile,[63,64] which was made by cyanation of *trans*-2-bromocyclohexanol,[81] according to the known procedure.[82,83]

Bis-2-cyclohexen-1-yl was obtained by the reaction of 3-bromocyclohexene and metallic sodium in ether by stirring at room temperature for several days, bp 120–125 °C (25 mm) [lit.[14] bp 106–107 °C (10 mm)].

Potentiostatic Oxidations of Cyclohexene. The anolyte (50 mL) was made up of various amounts of cyclohexene in 0.80 M methanolic sodium cyanide solution. The catholyte was a methanolic solution of sodium cyanide. The anode and cathode compartments were crudely purged with nitrogen in most experiments. This did not affect the electrode process. The reaction was carried out at a controlled anode potential at 25 °C. During the electrolysis, the solution was stirred magnetically. To the electrolyzed mixture were added internal standards for VPC analyses, the mixture was treated with water, and the organic material was extracted with ether. The ethereal solution was analyzed by VPC using a PEG 6000 column.

Each product was separated in pure form by preparative VPC and the IR and NMR spectra of the products were compared with those of the corresponding authentic sample. These products are listed below in order of increasing retention time: methoxycyclohexane, 3-methoxycyclohexene (**1**), dimethoxymethylcyclopentane (**2**), *trans*-1,2-dimethoxycyclohexane, isocyanocyclohexane (**5**), 3-isocyanocyclohexene (**3**), cyclohexanecarbonitrile (**6**), 2-cyclohexene-1-carbonitrile (**4**), bis-2-cyclohexen-1-yl (**8**), *trans*-2-methoxycyclohexanecarbonitrile (**7**), and unidentified minor components.

Solvolysis of *trans*-2-Cyanocyclohexyl Tosylate in Methanolic Cyanide Solution. Solvolysis of *trans*-2-cyanocyclohexyl tosylate (0.28 g, 0.001 mol) was carried out in 20 mL of methanolic sodium cyanide solution (0.1 M) at room temperature for several days. The reaction mixture was treated with water and the organic material was extracted with ether. The ether was removed by distillation under reduced pressure. VPC analysis showed only the presence of 1-cyclohexene-1-carbonitrile. Neither 2-cyclohexene-1-carbonitrile nor *trans*-2-methoxycyclohexanecarbonitrile was detected.

Acknowledgment. This work was partially supported by a grant from the Ministry of Education.

Registry No.—**1,** 2699-13-0; **2,** 20117-79-7; **3,** 62126-66-3; **4,** 13048-17-4; **5,** 931-53-3; **6,** 766-05-2; **7,** 62126-67-4; **8,** 1541-20-4; cyclohexene, 110-83-8; sodium cyanide, 143-33-9; *trans*-2-cyanocyclohexyl tosylate, 62126-68-5.

References and Notes

(1) K. Yoshida and S. Tsutsumi, *Tetrahedron Lett.*, 2501 (1966).
(2) V. D. Parker and B. E. Burgert, *Tetrahedron Lett.*, 4065 (1965).
(3) L. Eberson and S. Nilsson, *Discuss. Faraday Soc.*, **45**, 242 (1968).
(4) K. Yoshida and T. Fueno, *Bull. Chem. Soc. Jpn.*, **42**, 2411 (1969); *J. Org. Chem.*, **36**, 1523 (1971).
(5) S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, **91**, 4181 (1969).
(6) K. Yoshida, T. Saeki, and T. Fueno, *J. Org. Chem.*, **36**, 3673 (1971).
(7) K. Yoshida and T. Fueno, *J. Org. Chem.*, **37**, 4145 (1972).
(8) N. L. Weinberg, D. H. Marr, and C. N. Wu, *J. Am. Chem. Soc.*, **97**, 1499 (1975).
(9) K. Yoshida, *J. Am. Chem. Soc.*, **98**, 254 (1976).
(10) W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).
(11) I. A. Avrutskaya and M. Ya. Fioshin, *Electrokhimiya*, **2**, 920 (1966); *Chem. Abstr.*, **65**, 14838*f* (1966).
(12) E. K. Spicer and H. G. Gilde, *Chem. Commun.*, 373 (1967).
(13) C. Pierre, *C. R. Acad. Sci., Ser. C*, **226**, 1703 (1968); *Chem. Abstr.*, **69**, 56441m (1968).
(14) A. J. Baggaley and R. Brettle, *J. Chem. Soc. C*, 2055 (1968).
(15) R. Brettle and J. R. Sutton, *J. Chem. Soc., Perkin Trans. 1*, 1947 (1975).
(16) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).
(17) G. Faita, M. Fleischmann, and D. Pletcher, *J. Electroanal. Chem.*, **25**, 455 (1970).
(18) M. Fleischmann and D. Pletcher, *Chem.-Ing.-Tech.*, **44**, 188 (1972).
(19) D. B. Clark, M. Fleischmann, and D. Pletcher, *Electroanal. Chem. Interfac. Electrochem.*, **42**, 133 (1973).
(20) T. Shono and A. Ikeda, *Tetrahedron Lett.*, 6207 (1968); *J. Am. Chem. Soc.*, **94**, 7892 (1972).
(21) H. Schäfer, *Chem.-Ing.-Tech.*, **41**, 179 (1969); **42**, 164 (1970).
(22) H. Schäfer and E. Steckhan, *Chem.-Ing.-Tech.*, **44**, 186 (1972).
(23) H. Schäfer and R. Pistorius, *Angew. Chem., Int. Ed. Engl.*, **11**, 841 (1972).
(24) K. K. Barnes and C. K. Mann, *J. Org. Chem.*, **32**, 1474 (1967).
(25) L. Papouchado, R. N. Adams, and S. W. Feldberg, *J. Electroanal. Chem.*, **21**, 408 (1969).
(26) N. L. Weinberg, *Chemtech.*, **4**, 184 (1974).
(27) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).
(28) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).
(29) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
(30) D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970).
(31) D. A. Demeo and A. J. Yencha, *J. Chem. Phys.*, **53**, 4536 (1970).
(32) G. Hentrich, E. Gunkel, and M. Klessinger, *J. Mol. Struct.*, **21**, 231 (1974).
(33) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2576 (1969).
(34) R. Lesclaux, S. Searles, L. W. Sieck, and P. Ausloos, *J. Chem. Phys.*, **53**, 3336 (1970).
(35) A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, **40**, 3338 (1975).
(36) G. Bodennec, A. Laurent, E. Laurent, and M. Thomalla, Extended Abstracts, Spring Meeting of the Electrochemical Society, Washington, D.C., May 1976, No. 76-1, p 770.
(37) D. Y. Myers, G. G. Stroebel, B. R. Ortiz de Montellano, and P. D. Gardner, *J. Am. Chem. Soc.*, **95**, 5832 (1973); **96**, 1981 (1974).
(38) J. Cornelisse and E. Havinga, *Chem. Rev.*, **75**, 353 (1975).
(39) Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 407 (1975).
(40) K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 553 (1975).
(41) A. Yoshino, K. Yamasaki, T. Yonezawa, and M. Ohashi, *J. Chem. Soc., Perkin Trans. 1*, 735 (1975).
(42) T. Austad, J. Songstad, and L. J. Stangeland, *Acta Chem. Scand.*, **25**, 2327 (1971).
(43) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).
(44) M. L. Herz, D. Feldman, and E. M. Healy, *J. Org. Chem.*, **41**, 221 (1976).
(45) K. Yoshida and T. Fueno, *Chem. Commun.*, 711 (1970); *J. Org. Chem.*, **38**, 1045 (1973).
(46) K. Yoshida, M. Shigi, and T. Fueno, *J. Org. Chem.*, **40**, 63 (1975).
(47) H. Meinert and D. Cech, *Z. Chem.*, **12**, 291 (1972).
(48) L. Eberson and B. Helgee, *Acta Chem. Scand., Ser. B*, **29**, 451 (1975).
(49) K. Koyama, T. Susuki, and S. Tsutsumi, *Tetrahedron*, **23**, 2675 (1967).
(50) T. Susuki, K. Koyama, A. Omori, and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **41**, 2663 (1968).
(51) V. D. Parker and L. Eberson, *J. Chem. Soc., Chem. Commun.*, 441 (1972).
(52) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(53) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967).
(54) T.-L. Ho, *Chem. Rev.*, **75**, 1 (1975).
(55) L. Eberson, *J. Chem. Soc., Chem. Commun.*, 826 (1975).
(56) K. Yoshida and S. Tsutsumi, *Tetrahedron Lett.*, 2417 (1965); *J. Org. Chem.*, **31**, 3835 (1966).
(57) H. J. Shine and C. V. Ristagno, *J. Org. Chem.*, **37**, 3424 (1972).
(58) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972).
(59) J. F. Evans and H. N. Blount, *J. Org. Chem.*, **41**, 516 (1976).
(60) H.-J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).
(61) A. E. Osterberg, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 185.
(62) D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969).
(63) M. Mousseron, J. Jullien, and F. Winternitz, *Bull. Soc. Chim. Fr.*, 878 (1948); *Chem. Abstr.*, **43**, 588*e* (1949).
(64) M. Mousseron, F. Winternitz, and J. Jullien, *C. R. Acad. Sci.*, **226**, 91 (1948); *Chem. Abstr.*, **42**, 3336*f* (1948).
(65) A. J. Vogel, *J. Chem. Soc.*, 1809 (1948).
(66) G. E. Lienhard and T.-C. Wang, *J. Am. Chem. Soc.*, **91**, 1146 (1969).
(67) O. Grummitt, J. Liska, and G. Greull, *Org. Synth.*, **44**, 26 (1964).
(68) H. Gilman and W. E. Catlin, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 188.
(69) H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).
(70) C. H. Tilford, M. G. Van Campen, Jr., and R. S. Shelton, *J. Am. Chem. Soc.*, **69**, 2903 (1947).
(71) L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, **9**, 399 (1926).
(72) I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim, and F. Rosendahl, *Org. Synth.*, **41**, 13 (1961).
(73) K. Ziegler and A. Späth, *Justus Liebigs Ann. Chem.*, **551**, 110 (1942).
(74) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 315 (1949).
(75) H. Adkins and A. K. Roebuck, *J. Am. Chem. Soc.*, **70**, 4041 (1948).
(76) A. R. Hanze, T. W. Conger, E. C. Wise, and D. I. Weisbalt, *J. Am. Chem. Soc.*, **70**, 1253 (1948).
(77) M. Mousseron, F. Winternitz, J. Jullien, and R. Jacquier, *Bull. Soc. Chim. Fr.*, 79 (1948); *Chem. Abstr.*, 42, 4951*d* (1948).
(78) G. Magnusson and S. Thorén, *J. Org. Chem.*, **38**, 1380 (1973).
(79) S. Moon and C. R. Ganz, *J. Org. Chem.*, **35**, 1241 (1970).
(80) H. L. Jackson and B. C. McKusick, *Org. Synth.*, **35**, 35 (1955).
(81) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942).
(82) L. Palfray and S. Sabetay, *Bull. Soc. Chim. Fr.*, **43**, 895 (1928).
(83) D. S. Noyce, G. L. Woo, and B. R. Thomas, *J. Org. Chem.*, **25**, 260 (1960).