FREE RADICAL REACTIONS IN ORGANIC ELECTRODE PROCESSES—IV

ANODIC OXIDATION OF CYANIDE IONS IN THE PRESENCE OF AROMATIC HYDROCARBONS†

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Abstract—Anodic oxidation of sodium cyanide in methanol has been carried out at a Pt anode in the presence of 1,2,3,4-tetrahydronaphthalene, naphthalene or anthracene. 1,2,3,4-Tetrahydronaphthalene added as organic substrate afforded 6-cyano-1,2,3,4-tetrahydronaphthalene and 1-methoxy-1,2,3,4-tetrahydronaphthalene. In the electrolysis between a Pt anode and a Hg-pool cathode in the presence of naphthalene and anthracene, yielded 1-cyanonaphthalene and 9-cyanoanthracene, respectively. The possible pathways are discussed.

THE electrolytic oxidation of the cyanide ion at a Pt anode in the presence of aromatic compounds[1] gives rise to cyanation of the aromatic nucleus. It is suggested that the active intermediate produced during electrolysis is an electrophilic radical, although alternative explanation may be given for this anodic aromatic cyanation.

Several reports on the anode reaction of cyanide ions,[2-5] which were carried out in water, liquid ammonia and pyridine using various anode materials, indicate that discharge of cyanide ions at the anode yields cyano radicals as active intermediates

$$CN^- \rightarrow \cdot CN + e^-$$
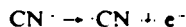
The radicals so formed could by coupling yield cyanogen or paracyanogen as observed in the reaction of silver cyanide in pyridine solution at platinum or tantalum anodes, or attack on the anode could give rise to metal cyanides. In the presence of organic substrates, the cyano radicals, if formed, could give rise to either substitution or addition to double bonds as observed in free radical reactions,[6] although it has been reported that anodic cyanation of organic compounds did not occur during the electrolysis of cyanide ions at a Pt anode in pyridine solution.

The choice of anhydrous organic solvents for organic electrode reactions is limited, because of the low solubility of inorganic electrolytes in these solvents, their

* Part III, K. Koyama, T. Susuki and S. Tsutsumi, *Tetrahedron* 23, 2665 (1967).

† Presented partly at *the 17th Annual Meeting of the Chemical Society of Japan.* Tokyo, April (1964).

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[1] K. Koyama, T. Susuki and S. Tsutsumi, *Tetrahedron Letters* No. 11, 627 (1965).
[2] H. Schmidt and H. Meinert, *Z. Anorg. u. Allgem. Chem.* 293, 214 (1957).
[3] H. Schmidt and H. Meinert, *Z. Anorg. u. Allgem. Chem.* 295, 156 (1958).
[4] H. Schmidt and H. Meinert, *Z. Anorg. u. Allgem. Chem.* 295, 174 (1958).
[5] D. T. Sawyer and J. J. Day, *J. Electroanal. Chem.* 5, 195 (1963).
[6] C. Walling, *Free Radicals in Solution* pp. 239 and 347. Wiley, New York (1957).

conductance of an electric current, and stability toward electrolytic reactions. Some cyanides, such as silver and cuprous cyanides,[7] are insoluble in water, slightly soluble in acetonitrile and soluble in basic solvents, while alkali metal cyanides, e.g. sodium and potassium cyanides are soluble or alcohols.

Initially, acetonitrile was chosen as solvent and cyclohexene as organic substrate. Unfortunately, the electrolysis of both acetonitrile solutions of cuprous and silver cyanides in the presence of cyclohexene failed to give detectable amounts of products. Similarly, experiments with silver cyanide in pyridine solution containing cyclohexene failed.

It has been shown that 1,3-butadienes are good radical acceptors,[8-10] and undergo additive dimerization with the radicals generated by the discharge of acetic acids. The electrolysis of cuprous cyanide in liquid ammonia containing butadiene was carried out between a Pt anode and a Cu cathode. Again no product was isolated. The possibility that butadiene might undergo an electrochemical cyanation under certain conditions, was shown in the electrolysis with silver cyanide in pyridine solution between a Pt anode and a Ag cathode in the presence of butadiene. The IR spectrum of the crude product (traces) exhibited the characteristic band assignable to a cyano group at near 2240–2260 cm^{-1} but the product was not characterized.

The anode reaction of sodium cyanide in methanol was next studied in the presence of various organic substrates. The reaction of cyanide ion at Pt electrodes was carried out in a mixture of hydrogen cyanide, butadiene and methanol containing sodium cyanide. After the usual work-up, a fraction which displayed at least four peaks on its vapor phase chromatogram was isolated. The IR bands at 1110, 1670, 2180 and near 2240 cm^{-1} indicated the possibility of methoxylation and cyanation reactions. Although the presence of an isonitrile was indicated, the amount was insufficient for identification.

The first successful experiments performed in the presence of 1,2,3,4-tetrahydronaphthalene. The conditions employed there were similar to those used for butadiene in methanol. Anode reaction of sodium cyanide in a mixture of hydrogen cyanide and 1,2,3,4-tetrahydronaphthalene in methanol afforded 6-cyano-1,2,3,4-tetrahydronaphthalene (I) and 1-methoxy-1,2,3,4-tetrahydronaphthalene (II).
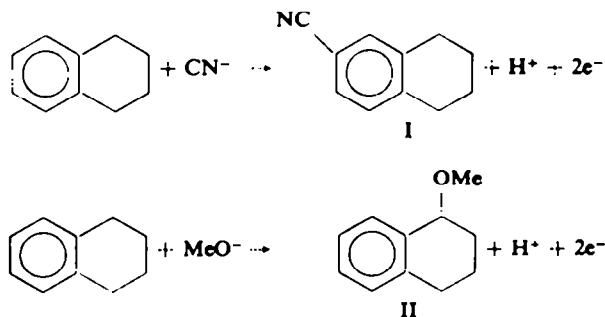
[7] e.g., *The Merck Index of Chemicals and Drugs* (7th Edition) pp. 303, 840, 936 and 950. Merck, Rathway, New Jersey (1960).
[8] M. S. Kharasch, P. G. Holton and W. Nudenberg, *J. Org. Chem.* 19, 1600 (1954).
[9] W. B. Smith and H. -G. Gilde, *J. Am. Chem. Soc.* 81, 5325 (1959).
[10] R. V. Lindsey, Jr. and M. L. Peterson, *J. Am. Chem. Soc.* 81, 2073 (1959).

The nitrile was identified after hydrolysis as 1,2,3,4-tetrahydro-6-naphthoic acid (III) by mixed m.p., elemental analysis and comparison of the IR spectrum with that of an authentic sample prepared by catalytic hydrogenation of β-naphthoic acid. Evidence for the formation of other isomeric acid could not be obtained by comparison of the IR spectra obtained before and after recrystallization.

The identification of 1-methoxy-1,2,3,4-tetrahydronaphthalene (II) separated by chromatography was performed by VPC and IR analyses.

The use of an excess hydrogen cyanide complicated the work-up of reaction mixtures by formation of polymeric materials and the necessity of prolonged removal of volatile products even though it was anticipated that excess hydrogen cyanide would promote the reaction in a manner observed in the Kolbe electrolysis in which the sodium liberated at the cathode reacts with the solvent, and the resulting alkali neutralizes some of the excess acid.

It is evident that the solvent can also participate in the anode reaction in a manner similar to the anodic methoxylation of aromatic hydrocarbons.[11] Therefore, 1-methoxy-1,2,3,4-tetrahydronaphthalene (II) may be formed by the action of methoxy radicals generated at the anode on 1,2,3,4-tetrahydronaphthalene i.e.
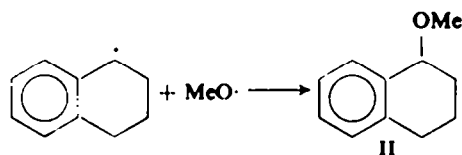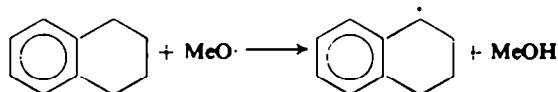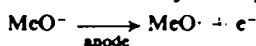

or
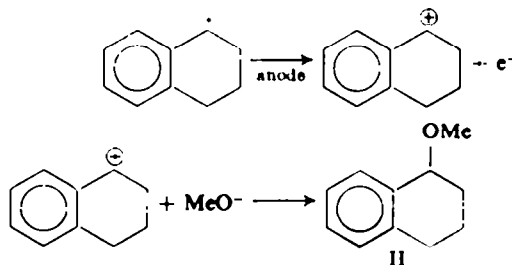
It was observed that substitution with the cyano group took place only on the aromatic nucleus in contrast to the anodic methoxylation of 1,2,3,4-tetrahydronaphthalene, in which the benzylic hydrogen atoms were exclusively replaced by OMe groups. A similar tendency was observed in experiments with ethylbenzene and cumene added as organic substrates. These results will be described later.

As polynuclear aromatic hydrocarbons appear more reactive than benzene toward both homolytic and heterolytic substitutions, naphthalene and anthracene were chosen as organic substrates. In these two electrolyses, a Hg-pool cathode was employed in place of Pt in order to remove the Na liberated at the cathode as the amalgam.

[11] T. Inoue, K. Koyama and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **37**, 1597 (1964).

Sodium cyanide was electrolysed in methanol containing naphthalene under the conditions employed for 1,2,3,4-tetrahydronaphthalene. The crude product after chromatographic separation, yielded 1-cyanonaphthalene. 2-Cyanonaphthalene and methoxynaphthalenes could not be detected.

$$\text{(naphthalene)} + CN^- \longrightarrow \text{(1-cyanonaphthalene)} + H^{\cdot} + 2e^-$$
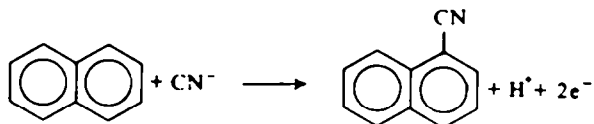
The product-analyses were performed by VPC, TLC, and comparison of IR spectra with those of authentic samples.

The electrolysis of the cyanide in methanol containing anthracene, afforded trace amounts of 9-cyanoanthracene together with considerable amounts of unidentified polymeric material. The nitrile was characterized by mixture m.p., and IR spectral comparison with an authentic sample. The thin layer chromatogram displayed a single spot corresponding in position to that of 9-cyanoanthracene.
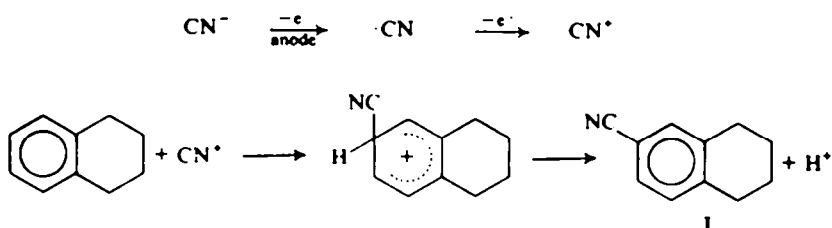
$$\text{(anthracene)} + CN^- \longrightarrow \text{(9-cyanoanthracene)} + H^+ + 2e^-$$
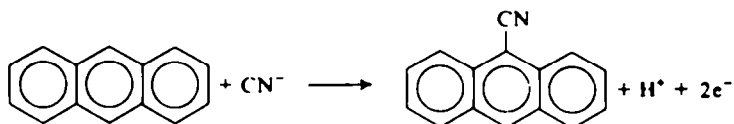
The authentic 9-cyanoanthracene was prepared by dehydration of the oxime.[12]

Polynuclear aromatic hydrocarbons having a low half-wave oxidation potential are easily adsorbed and oxidized at the anode to give the cation radicals which rapidly undergo further reactions,[13] and probably give rise to polymeric products.

At least three possible reaction pathways are conceivable for this anodic cyanation of aromatic compounds.

1. *Electrophilic substitution through generation of a cationic intermediate from the cyanide at the anode*

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

$$\text{(tetrahydronaphthalene)} + CN^+ \longrightarrow \text{(cationic intermediate)} \longrightarrow \text{(NC-substituted)} + H^+$$

I

The observed orientation in this anodic aromatic cyanation is analogous to the chlorination[14] in the presence of an Fe catalyst, sulfonation,[15] chloromethylation,[16] and the Friedel–Crafts alkylation and acylation[17] of 1,2,3,4-tetrahydronaphthalene affording mainly the 6-substituted products.

[12] L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.* **60**, 2555 (1938).
[13] K. E. Friend and W. E. Ohnesorge, *J. Org. Chem.* **28**, 2435 (1963).
[14] P. G. Harvey *et al.*, *J. Appl. Chem.* **4**, 325 (1954).
[15] *The Encyclopaedia of Organic Chemistry*, series III, 12 B, p. 59. Elsevier, Amsterdam (1948).
[16] Y. Abe and T. Masuda, *Org. Syntheses Japan*, **6**, p. 32. Gihodo, Tokyo (1953).
[17] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.* **339**, 343 (1936).

This reaction pathway depends on the cyanide ion at the anode undergoing a two electron transfer, with sufficient energy available for the electron transfer process. This, however, is unlikely since the value of 337 kcal (14·6 ev) for the ionization potential of the cyano radical[18] is too high to suggest the generation of such cationic intermediates, even though the gas-phase ionization potential is apparently lowered by adsorption and solvation effects, and some corrections to evaluate the half-wave oxidation potential of a cyano radical are necessary.[19]

2. *Homolytic aromatic substitution with the cyano radical generated by anodic oxidation of cyanide ion*

$$CN^- \xrightarrow[\text{anode}]{} \cdot CN + e^-$$
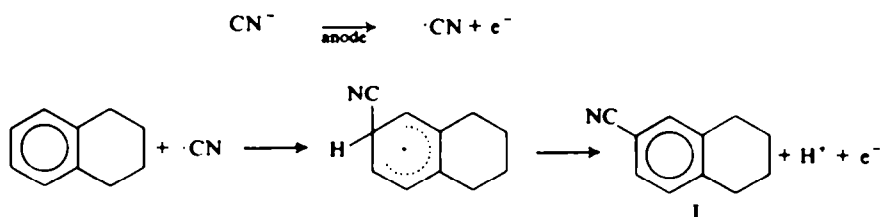
Recently, it was reported that the electron affinity of the cyano radical was 74 kcal (3·21 ev).[18] The radical having a relatively high electron affinity might attack the carbon-hydrogen bond, owing to polar contributions to the transition state.[20]

$$[R–H\ X\cdot \rightarrow R\cdot {}^+H\ X{:}^- \rightarrow R\cdot H–X]$$
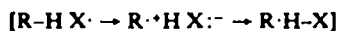
When the attacking radicals are electron-seeking ones, the electron availability of bonds in a substrate molecule plays an important role for determining which carbon-hydrogen bonds are attacked.

As the substitution by cyano groups took place on bonds with high electron density, it seems possible that polar effects may operate in this anodic aromatic cyanation.

3. *Discharge of the aromatic substrates at the anode leading to the formation of their ion radicals*

IV
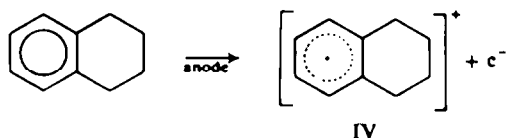
The polarographic oxidation of aromatic hydrocarbons have indicated that the anode reaction proceeds by generation of the cation radicals by loss of one π-electron from each molecule. The half-wave polarographic oxidation potentials of benzene, naphthalene and anthracene[21] are 2·08, 1·34 and 0·84 v (*vs.* Ag⁻/0·1 N Ag⁺), respectively.
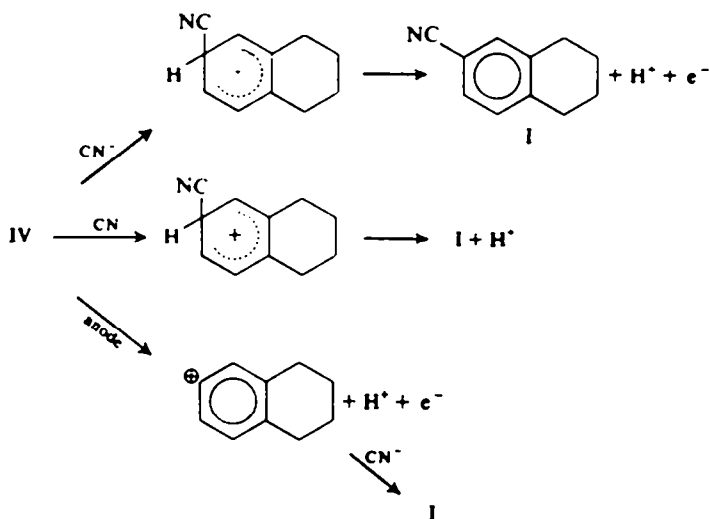
Therefore, the aromatic hydrocarbon may be oxidized to the cation radical which

[18] J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.* **82,** 1555 (1960).
[19] E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.* **85,** 2124 (1963).
[20] G. A. Russell, *J. Org. Chem.* **23,** 1407 (1958).
[21] W. C. Neikam and M. M. Desmond, *J. Am. Chem. Soc.* **86,** 4811 (1964).

then reacts either with the cyanide ion or radical and formation of the aromatic nitrile. A similar mechanism was proposed[22] and recently developed[23-25] for the anodic acetoxylation and aroyloxylation of aromatic compounds. The present study, however, provides no definite support for this assumption, and further investigation will be necessary to establish the mechanism of the reaction.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra: Shimadzu IR spectrophotometer IR-27C. VPC analysis: Toyo gas chromatograph GC-S-7.

Materials. Naphthalene was purified by sublimation, and then recrystallized, m.p. $81 \cdot 5°$ (MeOH). Commercially available anthracene was purified through an alumina column, and then recrystallized from alcohol, m.p. 217°. MeOH (reagent grade) was distilled from CaH_2. Other chemicals were reagent grade quality.

Electrolysis of a solution of sodium cyanide and 1,2,3,4-tetrahydronaphthalene in methanol. A mixture of NaCN (5 g), HCN (20 ml), 1,2,3,4-tetrahydronaphthalene (78 g, 0·6 mole) and MeOH (150 ml, 120 g) was electrolysed between 2 parallel Pt electrodes having an area of $2 \cdot 5 \times 6 \cdot 0$ cm² for the anode and $8 \cdot 0 \times 5 \cdot 0$ cm² for the cathode, spaced ca. $1 \cdot 0$ cm apart, at 5–10° ($4 \cdot 0$ v at 0·5 amp). The contents were stirred magnetically, and N was bubbled through the mixture during electrolysis which was continued until 0·5 faraday had been passed through the cell. After removal of MeOH under red. press., and inorganic cyanide by filtration, the oily products were distilled to give the following fractions: (A), wt. 19 g, b.p. 40–65° at 4 mm; (B), 16·5 g, b.p. 65–93° at 4 mm; (C), 8·0 g, b.p. 93–121° at 4 mm; (D), 3·0 g, b.p. 121–150° at 4 mm.

IR analysis suggested the presence of a methoxylated product in each fraction. Moreover, IR spectra of fractions C and D exhibited an absorption band assignable to a cyano group at 2250 cm⁻¹. Accordingly, a fifth part of each fraction was combined, dissolved in benzene and the soln chromatographed on alumina. Elution with benzene gave II (2 g). Further distillation of II gave an analytical sample, b.p. 64–65° (0·8 mm), n_D^{15} 1·5366. The IR spectrum agreed with that obtained previously.[11] The VPC on 25% polyethylene glycol 6000 on Shimalite (equiv to Chromosorb P) at a column temp of 164° with H_2 as carrier gas (0·7 kg/cm²) showed only a single peak with the same retention time

[22] L. Eberson, *Acta Chem. Scand.* 17, 2004 (1963).
[23] M. Leung, J. Herz and H. W. Salzberg, *J. Org. Chem.* 30, 310 (1965).
[24] S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Am. Chem. Soc.* 86, 4139 (1964).
[25] K. Koyama, K. Yoshida and S. Tsutsumi, *Bull. Chem. Soc. Japan* 39, 516 (1966).

(17 min) as that of an authentic sample. Total yield of II was 10 g. (Found: C, 81·27; H, 8·81. Calc. for $C_{11}H_{14}O$: 81·44; H, 8·70%.)

Half portions of fractions C and D were combined and hydrolysed with 75% H_2SO_4, yielding 0·7 g of a white solid, m.p. 145-150°. After recrystallization from acetone–water, III, m.p. 152-153°, was identified with an authentic sample prepared by hydrogenation of 2-naphthoic acid with Raney Ni (IR and mixed m.p.). Total yield (1·4 g) of III corresponds to 1·3 g of I. No evidence for the presence of the other isomeric acids could be provided by comparison of the IR spectra obtained before and after recrystallizations of III. (Found: C, 74·80; H, 6·70. Calc. for $C_{11}H_{12}O_2$: C, 74·97; H, 6·86%.)

Electrolysis of a solution of sodium cyanide and naphthalene in methanol. To a soln of NaCN (14·2 g) in MeOH (300 ml, 240 g), naphthalene (5·1 g, 0·04 mole) was added. Electrolysis of the soln was carried out between a Pt anode (5·0 × 6·0 cm) and a Hg-pool cathode (a surface area of ca. 50 cm²) at 0–5° (with 5–6 v at 1 amp and with 0·55 faraday passed). Magnetic stirring was maintained, and a continuous stream of N_2 flowed through the soln during electrolysis.

As the reaction proceeded, NaCN (23·1 g) was added portionwise. After removal of the solvent under red. press., the residue was dissolved in benzene, and washed with water to remove the unchanged cyanide. The benzene layer was dried over $MgSO_4$, and then evaporated under red. press. to yield 5·6 g of a dark brownish residue. This gave at least 4 spots (TLC). A portion (1·9 g) of the residue was chromatographed on silica gel (60 g) and eluted with benzene. Fractions (50–100 ml each) were collected and evaporated to dryness under red. press., and the residues examined by TLC, and combined on the basis of chromatographic behaviour.

The first combined residues (0·35 g) gave a single peak with the same retention time (9·2 min) as that of 1-cyanonaphthalene (VPC: 25% Silicone High Vacuum Oil on Shimalite, 2 m; column temp, 206°; carrier gas, He, 27 ml/min). The residues also displayed (TLC) only one spot at a position identical with that of an authentic sample. Moreover, the IR spectrum was identical with that of an authentic sample exhibited a band at 2260 cm⁻¹ (cyano group). An attempt to convert the nitrile into 1-naphthoic acid by hydrolysis with alcoholic KOH was unsuccessful.

The second combined residues revealed (TLC) the presence of at least 2 components, and provided evidence for the absence of the methoxylated compounds, e.g. 1- and 2-methoxynaphthalenes, and 2-cyanonaphthalene. The components, which gave spots (TLC), were not further investigated.

Authentic 1- and 2-methoxynaphthalenes were prepared by action of Me_2SO_4 on the respective sodium naphtholates.

Electrolysis of a mixture of sodium cyanide and anthracene in methanol. A suspension of anthracene (4·5 g, 0·025 mole) in MeOH (300 ml) containing NaCN (15·8 g) was electrolysed at −1–3° (1 amp, 5 v and 10·5 hr). During electrolysis, NaCN (21·7 g) was added portionwise. After removal of the solvent, the residue was extracted with 450 ml benzene, and the benzene evaporated to dryness under red. press. leaving 4·7 g of crude product. This was chromatographed on alumina, and eluted with benzene. The eluates after evaporation of the solvent were combined on the basis of the IR data. The combined fraction which gave an IR spectrum displaying a band at 2260 cm⁻¹ was recrystallized from glacial AcOH yielding 0·04 g of yellow needles, m.p. 171–173°, identified with authentic 9-cyanoanthracene (mixed m.p., and IR spectrum).

Small quantities of yellow solid (m.p. higher than 240°) were obtained from the next combined fraction, but were not further investigated.

The 9-cyanoanthracene prepared,[16,16,17] m.p. 175–176°, gave an IR spectrum displaying major bands at 730, 782, 845, 900, 955, 1165, 1190, 1270, 1455 and 2260 cm⁻¹.

[16] L. F. Fieser and J. E. Jones, *Organic Syntheses* Vol. 20, p. 66. Wiley, New York (1940).

[17] L. F. Fieser, J. L. Hartwell and J. E. Jones, *Organic Syntheses* Vol. 20, p. 11. Wiley, New York (1940).