I. THE KOLBE SYNTHESIS OF HYDROCARBONS

II. NORTRICYCLENE FROM ISOMERIZED NORBORNENE

By

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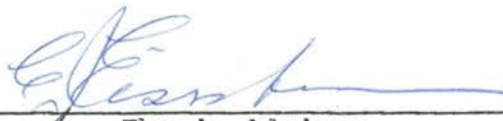
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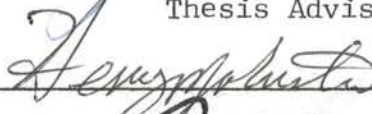for the degree of
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Dean of the Graduate School

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PART I. THE KOLBE SYNTHESIS OF HYDROCARBONS

I. INTRODUCTION

The synthesis of hydrocarbons by an electrochemical method was described in 1849 by Kolbe (1) who reported the formation of a symmetrical hydrocarbon and carbon dioxide on electrolysis of a sodium or potassium salt of a carboxylic acid. It was later discovered that a mixture of three different hydrocarbons (2) resulted from electrolysis of salts of a mixture of two carboxylic acids. Another important development was the synthesis of a diester (3) from the electrolysis of the half-ester of a dicarboxylic acid. In recent years the Kolbe electrochemical synthesis has been utilized to prepare natural products such as lipids (4).

The Kolbe synthesis may be carried out by dissolving a carboxylic acid in methanol containing sufficient sodium methoxide to neutralize a small portion of the acid. The solution is then electrolyzed between two platinum electrodes until the solution becomes alkaline which indicates the reaction is complete and most of the carboxylic acid has been consumed. The carboxylate ions are converted into hydrocarbon at the anode. At the cathode the liberated sodium reacts with the solvent to regenerate methoxide ion which neutralizes an equivalent of carboxylic acid. The process continues in this manner until all the starting material has been utilized.

Most Kolbe electrolytic reactions have been carried out with platinum foil electrodes not exceeding 2 x 4 cm. in area (4). The size of the electrode determines the scale of the reaction and it is not surprising that the earlier workers were limited to 2-25 g. of carboxylic acid in each reaction. No detailed investigation has been reported which describes modifying the electrodes to increase the area or to construct the electrodes of cheap and readily available materials which in turn would permit increase of area and consequently the scale of the operation.

Our aim in the present investigation was to develop large area electrodes and if possible, to develop a process which could be made to operate continuously. A step has been taken in this direction by preparation of platinum coated titanium electrodes. The electrode area for each electrode has been increased to 77.5 cm^2 as contrasted to 8 cm^2 previously reported (4). In addition we employ a sandwich of three electrodes which permits us to increase the total anode area to 155.0 cm^2.

II. REVIEW OF THE KOLBE ELECTROCHEMICAL SYNTHESIS

In his first electrochemical synthesis, Kolbe (1) obtained ethane and carbon dioxide at the anode during the electrolysis of an aqueous solution of potassium acetate.

$$2\ CH_3 - CO_2^- \xrightarrow{\ 2e\ } CH_3 - CH_3 + CO_2.$$
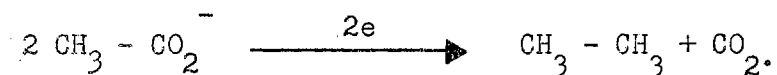
In 1855, Wurtz (2) extended the use of Kolbe synthesis to mixtures of two fatty acids and obtained products due to symmetrical and unsymmetrical coupling of the two components.

$$R - CO_2^- \quad + \quad R^1 - CO_2^-$$

$$R - R \quad + \quad R - R^1 \quad + \quad R^1 - R^1$$
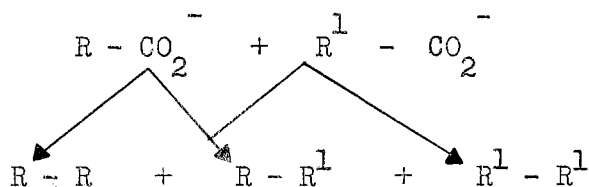
The next important development was the discovery by Brown and Walker (3) in 1891 that half esters of aliphatic dicarboxylic acids undergo the Kolbe reaction to give diesters of double the chain length less two carbon atoms.

$$2\ RO_2C-(CH_2)_n-CO_2^- \xrightarrow{\ 2e\ } RO_2C-(CH_2)_{2n}-CO_2R$$

Mechanism. The mechanism of the Kolbe reaction has been the subject of much discussion. Three mechanisms were proposed for the Kolbe reaction: (a) Peroxide Theory (5), (b) Hydrogen Peroxide Theory (5) (6), (c) Radical Theory (5).

Peroxide Theory. The Kolbe reaction is represented in the following manner:

$$
\begin{array}{ccccc}
R-CO_2^- \xrightarrow{-2e} R-CO_2 \longrightarrow R-COO \longrightarrow R^\cdot + CO_2 \longrightarrow R-R \\
R-CO_2^- \qquad R-CO_2^\cdot \qquad R-COO \qquad R^\cdot + CO_2 \qquad 2\,CO_2 \\
(A) \qquad\qquad (B) \qquad\qquad (C) \qquad\qquad (D) \qquad\qquad (E)
\end{array}
$$
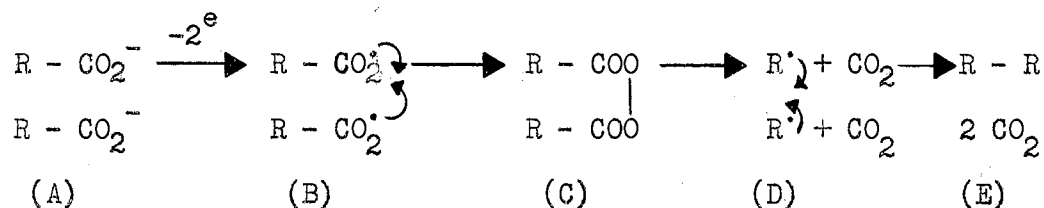
To account for by products by the Kolbe reaction, it has been suggested that the intermediate peroxides (c) undergo hydrolysis to give peracids which decompose to give alcohols.

$$
\begin{array}{c}
R-COO \\
| \longrightarrow \quad R-CO_2H \\
R-COO \qquad + \qquad \longrightarrow R-OH + CO_2 \\
\qquad R-CO_3H
\end{array}
$$
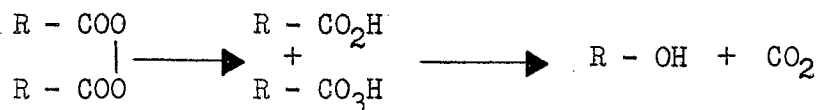
This theory has not received support for the formation of these intermediates.

Hydrogen Peroxide Theory. Electrolytic study of acetates by Glasstone and Hickling (6) suggested that hydrogen peroxide is first formed and reacts with acetate ions giving rise to ethane and carbon dioxide.

$$
2\,OH^- \longrightarrow H_2O_2 + 2e
$$
$$
H_2O_2 + 2\,CH_3CO_2^- \longrightarrow C_2H_6 + CO_2 + 2\,OH^-
$$
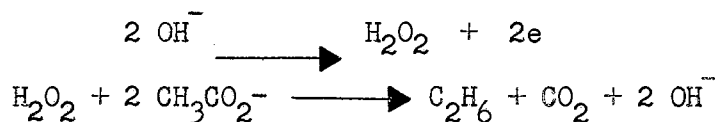
This theory was also abandoned because it requires presence of hydroxyl ions and, hence, applies only to electrolysis of aqueous solution.

Radical Theory. The most commonly accepted mechanism is the radical theory. It seems most probable that a sequence of three processes is involved at the anode (a) discharge of the carboxylate ions $R - CO_2^-$ to give carboxylate radicals, (b) rapid decarboxylation to give alkyl radicals which combine to yield the Kolbe product.

$$R - CO_2^- \xrightarrow{\;-e\;} R - CO_2^\cdot \longrightarrow R^\cdot + CO_2$$

$$2\,R^\cdot \longrightarrow R - R$$
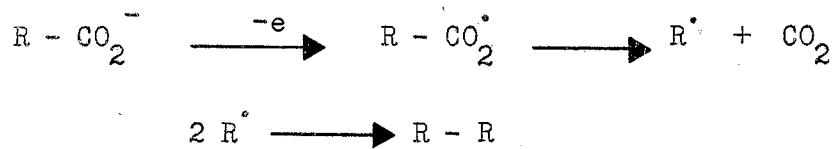
At the cathode methanol reacts with the sodium ion forming sodium methoxide (5).

$$2\,MeOH + 2\,Na^+ \xrightarrow{\;-2e\;} 2\,MeONa + H_2$$
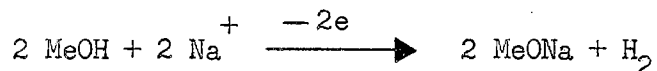
All the side reactions (olefins, parafins and alcohol) could be well explained through this free radical mechanism.

Aqueous and methanolic solutions have been used as solvents. Methanol has the advantage of being a superior solvent for most organic acids. Moreover, the experimental conditions for optimum yields (high carboxylate concentration, anodic current density and pH of the electrolyte) are less critical in methanolic than in aqueous medium (4) (5) (6) (7). A minor practical disadvantage in using methanol as solvent is that the resistance of the cell is greatly increased and more heat must be dissipated during the electrolysis. Another drawback is that small amounts of the starting materials, $R - CO_2H$, are converted into their methyl esters (8). However, other side reactions leading to alcohols (4), esters (4), and the corresponding olefins

(4) are much less in evidence in methanolic than in aqueous media.

An advantage of the Kolbe reaction is that organic compounds synthesized by this method have a specific stereochemistry. That is, asymmetric centers at beta or more remote positions are undisturbed during the reaction.

The Kolbe electrolytic synthesis has been applied not only to straight chain acids and half-esters but also to acids and esters containing alkyl, cyano, halo, keto and hydroxy groups substituted on a carbon other than alpha-carbons. The Kolbe syntheses with alpha-substituted carbon have been reported, but the yields are usually low. An important limitation of the Kolbe reaction is that neither alpha-beta nor beta-gamma-unsaturated acids undergo anodic coupling and in some cases considerable polymer is encountered with the double bond at more remote location.

In recent years Kolbe reactions have been employed in the synthesis of over forty natural products mostly lipids. Two notable early uses of symmetrical coupling were in the preparation of perhydrobixin and perhydrocrocetin (9). The synthesis of ($\pm$) muscone was one of the first applications of the Kolbe reaction in the field of natural products (10).

III. EXPERIMENTAL METHODS

Description of Small Platinum Electrodes and Their Use.
Small platinum electrodes are constructed from two sheets of
platinum foil 5.1 x 3.8 cm. The electrodes are fastened to 10
gauge platinum wire which in turn is connected to copper leads
through uranium glass seal as shown in Figure 1. The copper wire
leads are connected in turn to the commutator and D.C. circuit.
The reversal of polarity is required to free the electrodes of
hydrocarbon deposit. The electrodes are contained in a Pyrex
glass cylinder (14" x 3"). External cooling is provided by ice
water circulating around the cylinder by means of water pump. A
magnetic stirrer is used to stir the reaction mixture and help
dissipate heat.

Synthesis of Eicosane. Freshly cut sodium (1.0 g.) is dis-
solved in absolute methanol (300 ml.). Undecanoic acid (21.6 g.)
is then added to the methanol in the cell. Current (1 amp, 30
volts) is applied across the electrodes as shown in circuit dia-
gram (Figure 2). As the electrolysis proceed eicosane crystalizes
and a gradual drop of current is observed. After two hours the
commutator is started at 6. r.p.m. to change the polarity of the
electrodes.

TO COMMUTATOR

COPPER WIRE

PYREX GLASS TUBE

64 cm.

3·5 cm.

6 mm.

URANIUM GLASS

16 GAUGE
PLATINUM WIRE

2-3 mm.

PLATINUM ELECTRODE
7 x 5·3 cm.
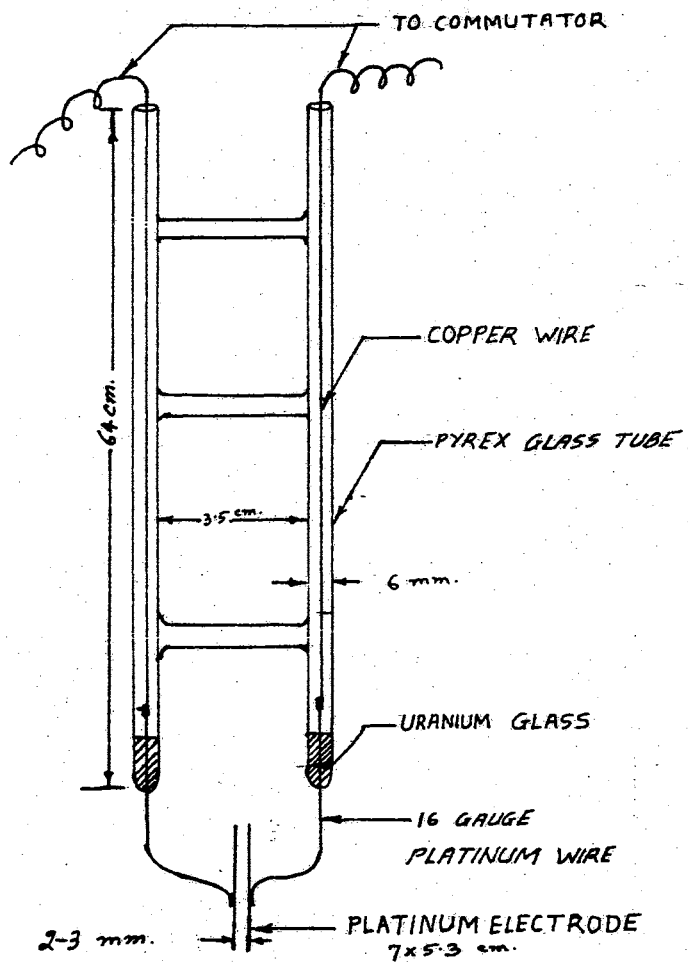
SMALL PLATINUM ELECTRODE

FIGURE 1

AMMETER

COMMUTATOR

D.C.

D.C. CIRCUIT

CELL
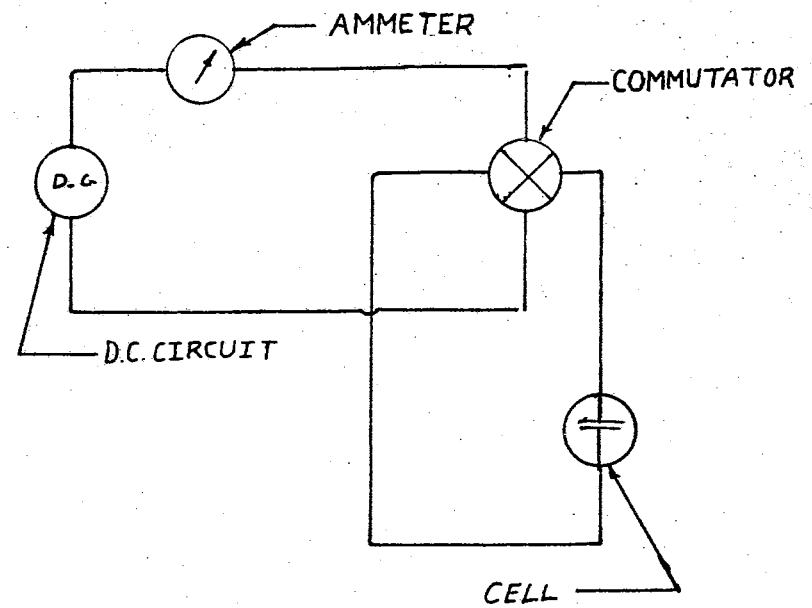
CIRCUIT DIAGRAM

FIGURE 2

The reaction mixture is tested several times during the electrolysis to check the pH by using two drops of reaction mixture, one drop of phenolphthalein and one drop of water on a spot plate. When the methanolic solution becomes basic, the reaction is stopped. Most of the methanol is evaporated and the residue is dissolved in ether. The ethereal solution is washed twice with 20 ml. of aq. 5% sodium hydroxide solution to remove any unreacted acid and thoroughly with water until the ether solution is neutral to pH paper. The solution is dried over anhydrous magnesium sulfate, filtered and evaporated to give 15.2 g. (92.8%) of eicosane. The alkali extract of ether solution is acidified with dilute hydrochloric acid solution and the liberated acid is filtered, washed with water and dissolved in ether. The ether solution is dried over anhydrous magnesium sulfate, filtered and after evaporation of ether there remains 2.6 g. (12.1% recovery) of undecanoic acid.

Commutator. The commutator is shown in Figure 3. It is an instrument which periodically reverses the polarity of the current passing through the electrolytic cell. It has four binding posts (1, 2, 3, and 4). Two of these for the input (from the power source) and the other pair for the output (to the cell). The commutator is mounted on Shaft A which is rotated mechanically by an electrical motor mounted as shown in Figure 4.

The central core (2-1/4" x 3" diam.) is made of an insulating phenolic laminated material, as are the parts C and G. The metal parts D, J and H are of copper, while the brush M is of graphite held by a clip to the end of a spring copper strip.
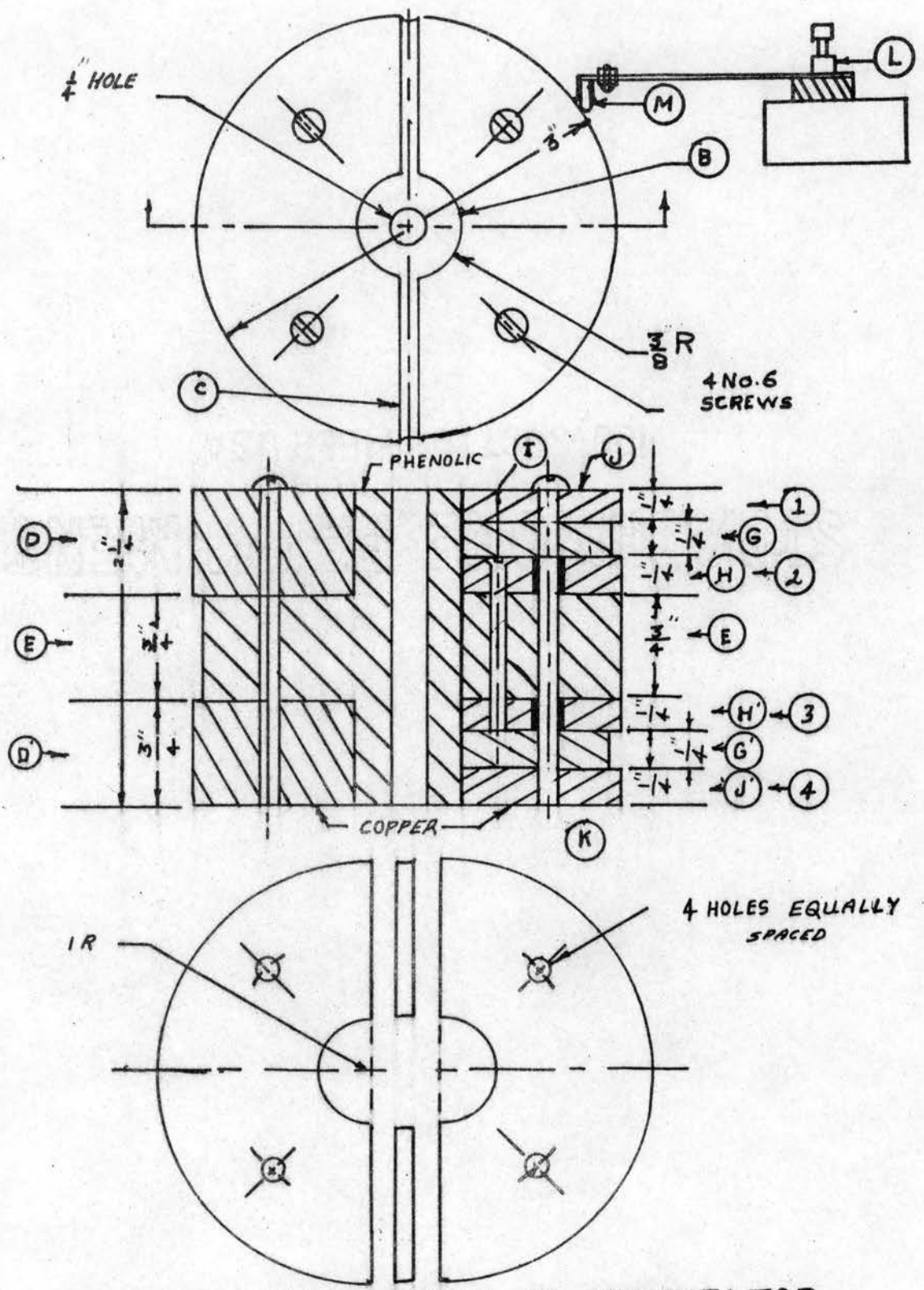
FIG.3 SECTIONAL DETAIL OF COMMUTATOR
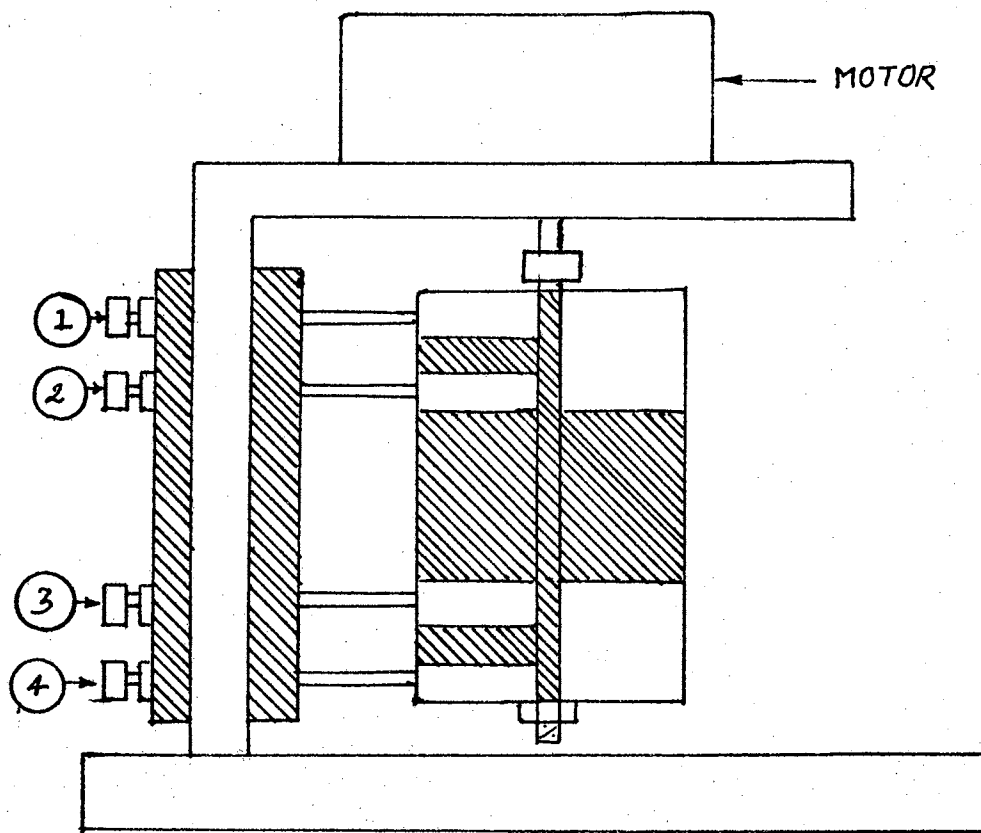
COMMUTATOR

FIGURE 4

A screw $\underline{I}$ connects brass pieces $\underline{HH}^1$ internally and acts as a means of electrical contact. Similarly a screw $\underline{K}$ connects $\underline{JJ}^1$ internally as a means of electrical contact. Screw $\underline{K}$ is electrically insulated from $\underline{HH}^1$ and thus prevents passage of current and rules out short circuit.

With D.C. current connected as input to $\underline{1}$ and $\underline{3}$ and output as $\underline{2}$ and $\underline{4}$ (Figure 3), then $\underline{1}$ and $\underline{4}$ are positive and $\underline{2}$ and $\underline{3}$ are negative. A 180° rotation of the commutator core produces a reversal of current polarity which results in $\underline{3}$ and $\underline{4}$ becoming negative while $\underline{1}$ and $\underline{2}$ are positive. The frequency with which the polarity is reversed depends upon the speed of the motor. Motors having $\underline{1}$ and $\underline{6}$ rotations per minute are used. The slower speed is more satisfactory.

Platinum Plated Copper Electrodes. Success with the small platinum electrodes encouraged us to investigate the development of large platinum plated electrodes of copper metal. Each electrode was 6" x 2" x 1/8" with a 10" x 5/8" x 1/8" attached side arm. (For similar figure see Figures 5 and 6). The electrodes were plated according to the formula given by E. C. Davis and R. A. Powell (11). However, the electroplated platinum chipped off and platinum black was deposited in some areas instead of platinum. These plated electrodes did not produce hydrocarbon.

Platinum Plated Titanium Electrodes. Mr. L. Greenspan (12) of Research and Development Division, Englehard Industries, Inc. arranged for constructing and plating titanium electrodes as shown

CLEAR HOLE NO. 8
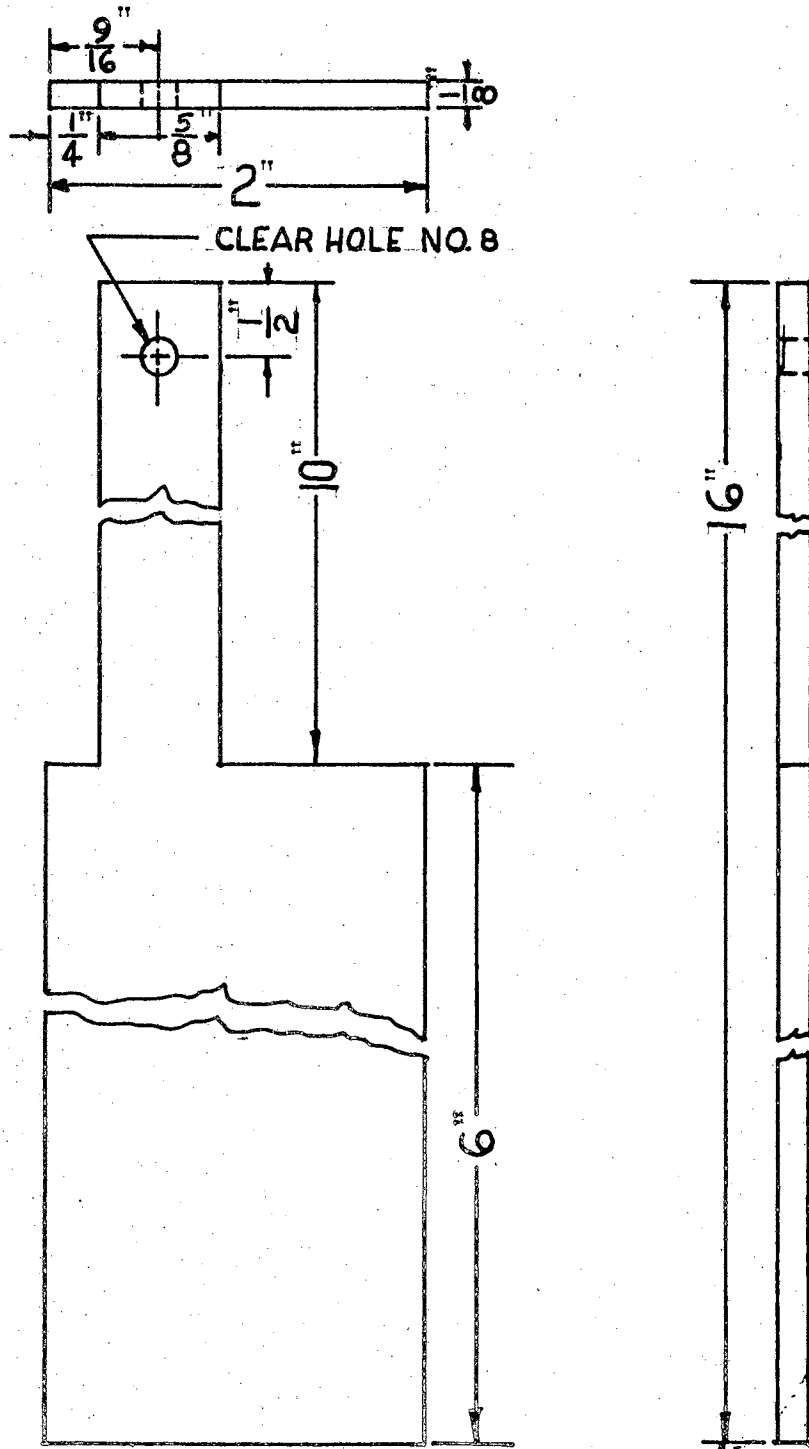
ELECTRODE
3 REQUIRED
FIGURE 5
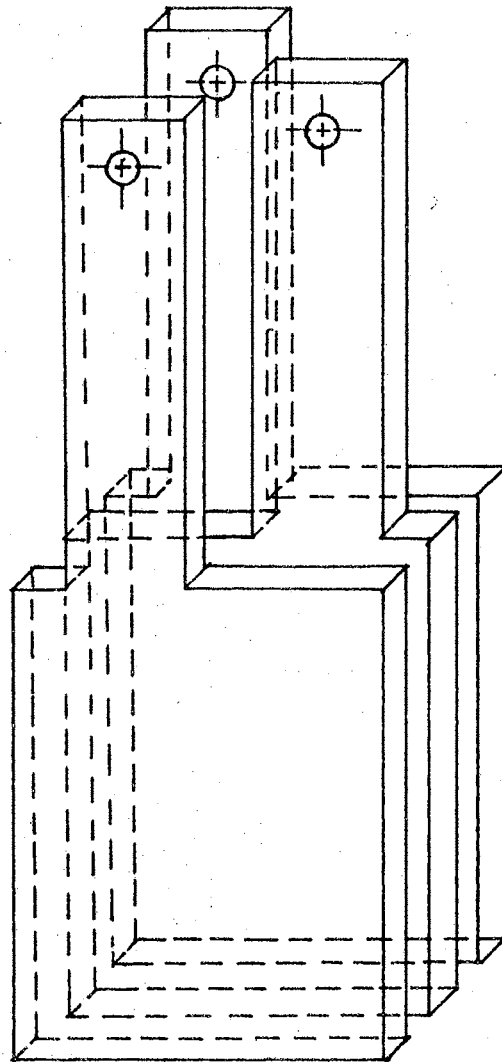
ELECTRODE ASSEMBLY

FIGURE 6

in Figures 5 and 6. The electrodes were electroplated with 250 microinches of platinum. They were supported and held in place on a phenolic disc (1/2" thick, 7" diameter) (Figure 7) with binding posts. A pyrex glass cylinder (18" x 6") was used as a cell. Two spacers made from Teflon sheet (1/16") were used to keep the electrodes at a fixed parallel distance of 5 mm. The side electrodes of the electrode sandwich were connected to one binding post to form the anode or the cathode depending on the polarity. The phenolic disc was held in place by three bolts which prevented accidental contact of electrode and cooling coil. The cooling coil was made of fourteen turns of 1/4" x 20' stainless steel tubing. Cold water from the cooling system was circulated through the cooling coil by means of a water pump. A 2" Teflon covered magnet was used to stir the reaction mixture.

Continuous Kolbe Electrolysis. The Kolbe electrolysis of lauric acid was converted from batch to semicontinuous operation by taking advantage of the insolubility of docosane in methanol. It was found that docosane would melt and rise to the surface if the reaction temperature were allowed to rise to 45-50° (m.p. of docosane is 44°). The molten hydrocarbon may then be withdrawn through a nylon tap inserted through the wall of the glass cylinder. Silicone rubber washers prevent leakage around the tap.

The results of a typical large scale semicontinuous runs are presented in Tables I and II. A continuous run involved 4 l. methanol, 1.45 g. potassium hydroxide (0.026 mole) and a total of

COOLING COIL APERTURES

ELECTRODE JUMPER

ELECTRODE

BINDING POST

LOCATING SCREWS

PHENOLIC RESIN
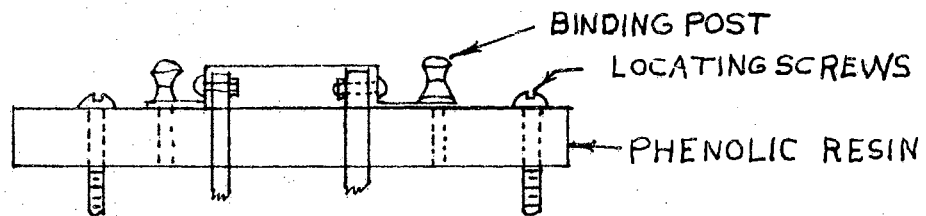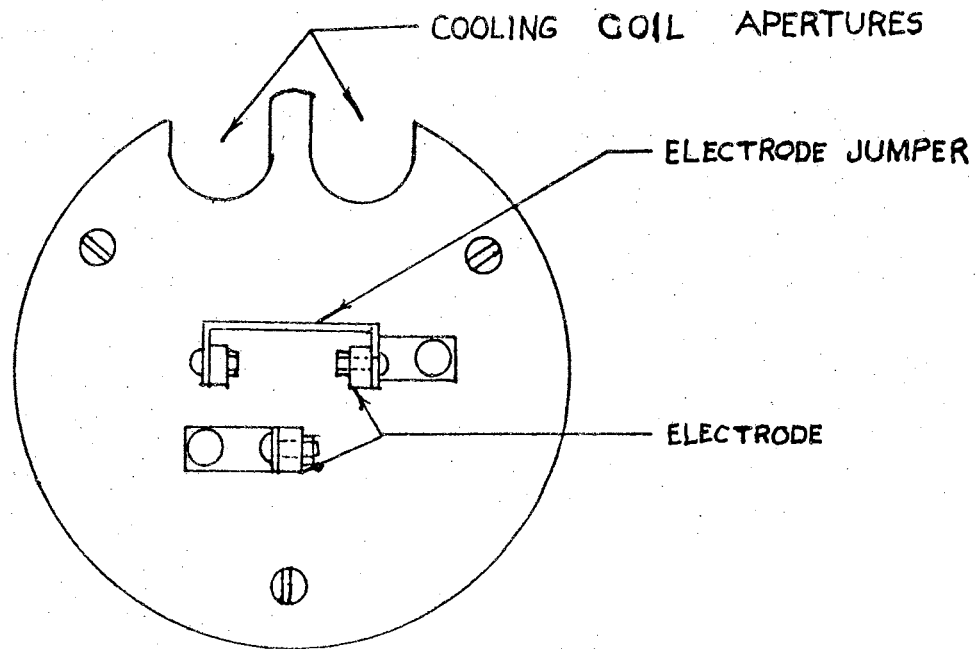
PHENOLIC DISC

FIGURE 7

TABLE I

SYNTHESIS OF DOCOSANE FROM LAURIC ACID

Expt. No.	Total Lauric Acid*	KOH or Na	Docosane Free From Lauric Acid	Side Prod- ucts	Lauric Acid Re- covered	% Yield of Docosane
1	50 g.	1 g.	23 g.	8 g.	10 g.	73%
2	200 g.	1.5 g.	83 g.	14 g.	73 g.	83%
3	400 g.	1.5 g.	236 g.	36 g.	19 g.	78%

*In ml. anhydrous methanol

TABLE II

CONTINUOUS SYNTHESIS OF DOCOSANE FROM LAURIC ACID BY KOLBE SYNTHESIS

Days Operation	0	1	2	3	4	5	6	7	8	9	10	11
Grams Crude Docosane	0	85	158	286	213	123	164	183	162	156	158	196
Grams Cumulative Docosane	0	85	243	526	742	865	1029	1212	1373	1529	1687	1883
Total Lauric Acid Added (In gms.)	400	200	200	200	200	200	200	200	200	200	200	200
Cumulative Grams Lauric Acid	400	600	800	1000	1200	1400	1600	1800	2000	2200	2400	2600

2600 g. of lauric acid. Lauric acid (400 g.) was added to initiate the reaction. At the end of each 24 hour period of electrolysis, the hydrocarbon was melted by allowing the reaction temperature to rise from 38-40° to 45-50°. The molten hydrocarbon was withdrawn and a fresh batch of lauric acid (200 g.) was added to the reaction mixture. The cycle was repeated eleven times.

IV. DISCUSSION

It has been demonstrated in the experimental work that bydrocarbons are easily synthesized by Kolbe electrochemical synthesis on a large scale. Platinum and iridium are the only known electrode metals which allow production of hydrocarbons in satisfactory yield. However, these metals are too expensive to use as massive electrodes and too flexible to use in thin sheets. Platinum plated copper electrodes were considered as a possibility. However, the plating is easily ruptured and once copper is exposed, the copper is attacked by the electrolytic solution, and dissolved into the reaction as cupric ions. This results in contamination of the electrolytic solution as well as destruction of electrodes.

Titanium metal is inactive to the electrolytic solution, is fairly rigid and easily plated with platinum. Electrodes formed from titanium were found to perform in a most satisfactory manner. In this case even if platinum becomes dissolved in the electrolytic solution its ions will not be transported.

The results of the synthesis of docosane from lauric acid using platinum plated titanium electrodes are shown in Table I.

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Table I shows the yield of hydrocarbon formation varies with the concentration of lauric acid.

V. CONCLUSION

The Kolbe synthesis of hydrocarbons from carboxylic acids may be carried out on a large scale if large area electrodes are developed. From our observation, it may be concluded that a semi-continuous operation could be developed for production of docosane. Production of other hydrocarbons on a semi-continuous basis would depend on solubility of hydrocarbon and acid in the selected solvent. The concentration of acid and temperature of operation would also require investigation in each case and these would be strongly influenced by the melting point of the hydrocarbon. In most cases the acid would be more soluble than the resulting hydrocarbon.

PART II. NORTRICYCLENE FROM ISOMERIZED NORBORNENE

I. INTRODUCTION

Tricyclo $\underline{/}$ 2.2.1.0^{2,6} $\underline{/}$ heptane (nortricyclene) a three membered bridged ring compound belonging to the tricyclo (2.2.1.0) heptane ring system is an isomer of bicyclo $\underline{/}$2.2.1$\underline{/}$-2-heptene (norbornene). It was first observed in 1934 by Komppa and Beckmann (13) that nortricyclene was found along with norbornene in the quinoline dehydrobromination of 2-exo-norbornyl bromide.

Later Alder and Rickert also obtained a mixture of norbornene and nortricyclene following the same procedure (14).

The reaction of phosphoric anhydride with 2-exo-norbornanol gave a mixture of 30% norbornene and 70% nortricyclene (15).

The first synthesis of nortricyclene was dehalogenation of dehydronorbornyl chloride using a n-amyl magnesium bromide (16). Roberts (16) also reported that nortricyclene is not affected by permanganate.

The preparation of nortricyclene from norcamphor hydrazone was patented in 1954 by N. V. de Bataafsche (British patent 712,278) (17). In 1955 Alder and co-workers (18) synthesized nortricyclene from norcamphor phenylhydrazone in about 37% yield.

25

It is known that exposure of bicyclo $\underline{/}$ 2.2.1 $\underline{/}$ heptanes to a variety of acidic reagents leads to olefines. The intermediates produced in these reactions are tricyclic in nature (19).

In 1958 Schleyer (20) reported the isomerization of norbornene to a mixture of nortricyclene and norbornene using synthetic silica-alumina catalyst (Houdry S-90).

We have studied the isomerization of norbornene using several silica-alumina catalysts. The best results were obtained with Houdry S-90 catalyst which caused isomerization of norbornene to a mixture of norbornene and nortricyclene. From this mixture, we were able to isolate pure nortricyclene by selectively destroying norbornene with potassium permanganate.

II. LITERATURE REVIEW

A general system of nomenclature has been developed to sup-
plement the many common and derived names given to bicyclic and
tricyclic compounds. In this general system, the number of car-
bons in each of the three bridges is noted and enclosed in brac-
kets; the numbers are arranged in decreasing order and separated
by periods. The term bicyclo and tricyclo appears immediately be-
fore the bracket, and prefixed to this term are the substituents,
the usual orders being applied. The total number of carbons in
the ring system is named, and the name appears immediately after
the bracket, note being taken of any carbon carbon double bonds
appearing in the ring system itself. The ring system is numbered
from the most highly substituted bridgehead position, and proceeds
around the largest ring in such a way as to give substituents the
lowest possible numbers. Carbons of the smallest bridge are then
numbered (21).

The terpene hydrocarbons have many bicyclic and tricyclic
members which must be named as previously mentioned. Our
examples, norbornene and nortricyclene, are compounds of this
type and are named as below (22):
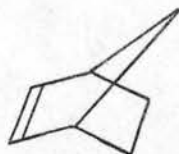
Bicyclo [2.2.1]-2-heptene
(Norbornene)
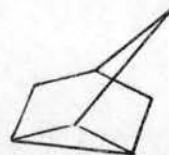
Tricyclo [2.2.1.0^{2,6}]-hep-
tane (Nortricyclene)

The history of nortricyclene parallels that of norbornene.
Komppa and Beckmann (13), Alder and Rickert (14) obtained a mix-
ture of norbornene-nortricyclene in the preparation of norbornene.
They were not aware at that time of the presence of nortricyclene,
but they did observe the oxidation of norbornene by potassium
permanganate was unusually slow. This is due to the presence of
nortricyclene which does not react with permanganate.

In 1941, Joshel and Butz (23) synthesized norbornene in
74% yield by a Diels-Alder reaction of ethylene and cyclopenta-
diene.

Nortricyclene was synthesized by J. D. Roberts, et al. (16),
N. V. de Bataafsche (17), and Alder and his co-workers (18).

In 1957, Schleyer isomerized norbornene to a mixture of
norbornene and nortricyclene containing 71% nortricyclene using
Houdry S-90 synthetic silica-alumina catalyst. He was able to
fractionally distill the mixture and isolate fractions containing
99% nortricyclene and 1% norbornene. Schleyer did not try oxidi-
zine the isomerized mixture even though it was known that nortricy-
clene is not affected by potassium permanganate (16). His investi-
gations were limited to studying the relative stability of norbor-
nene and nortricyclene.

III. EXPERIMENTAL

Isomerization of Norbornene with 1% Houdry S-90 Silica
Alumina Catalyst. A mixture of 50.0 g. of freshly distilled nor-
bornene (b.p. 96°) and 1.0 g. of silica alumina catalyst is heated
at reflux temperature. Samples are withdrawn from the reaction
flask at two hour intervals. The samples are analyzed on a 1/4"
x 7' column of acid-washed firebrick coated with 20% silicone
nitrile polymer (XE-60) using helium as the carrier gas at 65°.

Isomerization with Houdry S-46, S-65 and S-90 Silica-
alumina Catalyst. The silica-alumina catalysts are of three types
having identical chemical composition ($SiO_2/Al_2O_3 = 87.3/12.4$)
but varying in physical properties as shown in Table I. The cata-
lysts were kindly furnished by Houdry Process and Chemical Co.,
Philadelphia, Pa.

TABLE I

PHYSICAL PROPERTIES OF HOUDRY CATALYSTS

		S-90	S-65	S-46
Surface Area	m^2/g	425-450	375-400	290-315
Bulk Density	kg/l	0.53	0.54	0.62
Pellet Density	kg/l	0.84	0.86	0.99
Porosity	vol. %	65	60	57
Absorption	wt. %	77	65	58
Average pore size	A°	70	80	82

Three essentially identical experiments were carried out to determine which catalyst (S-90, S-65, or S-46) would be the most effective in isomerizing norbornene to nortricyclene. The results of these experiments using 1% of catalyst to total weight of nor-bornene are summarized in Table II.

TABLE II

ISOMERIZATION WITH HOUDRY S-46, S-65 AND S-90
SILICA-ALUMINA CATALYSTS

Catalyst	Wt. of Nor-bornene	% Nortricyclene After 8 Hours At Reflux	% Polymer After 8 Hours
S-46	155 g.	25	11
S-65	139 g.	27	6
S-90	160 g.	39	24

Isomerization with 5% Houdry S-90 Catalyst. Norbornene was isomerized with 5% S-90 catalyst in the same manner as described for experiments with 1% of catalyst. The reaction mixture was sampled at 0.5 hour intervals with first sample taken after two hours heating at reflux temperature. The temperature of the refluxing reaction mixture was found to vary depending on the composition of the isomerized mixture. Two typical runs using 86 g. and 183 g. norbornene gave 46 g. and 100 g. equilibrated mixture of norbornene and nortricyclene (28/72 and 29/71) and 34.0 g. and 61.0 g. of polymer after heating at the reflux temperature for 3.5 hours. These data are presented in Table III.

TABLE III

ISOMERIZATION WITH 5% HOUDRY S-90 CATALYST

Hours	Temp. of Reaction Flask	% Nor-tricyclene	% Polymer
2.0	101.2	59	-
2.5	102.7	64 (58)	-
3.0	103.8 (102.5)	71 (67)	-
3.5	104.9 (103.0)	72 (72)	40 (33)

Isomerization With 1-2% Houdry S-90 Catalyst. It was ob-
served by Schleyer (21) that the Houdry S-90 catalyst becomes
poisoned after two hours and it, therefore, became necessary to
change the catalyst for further isomerization of norbornene.

The results of our studies in the replenishing of Houdry
S-90 catalyst are reported in Table IV.

Oxidation With Potassium Permanganate. It has been ob-
served that oxidation of norbornene with potassium permanganate
gives cis-1,3-cyclopentane dicarboxylic acid (24) and nortricy-
clene is reported to be unaffected by potassium permanganate (16).

A mixture containing 51.4 g. (0.55 moles) of isomerized
mixture of norbornene and nortricyclene (29/71), 60.0 g. (0.38
moles) of potassium permanganate and 1.5 l. of water is heated to
60-65° with vigorous stirring. An additional 55.0 g. (0.37 moles)
of potassium permanganate is added to the reaction mixture in
small portions. Complete oxidation of norbornene is assumed since

TABLE IV

EQUILIBRATION OF NORBORNENE WITH HOUDRY S-90 CATALYST

Norbornene Initial Wt.	Grams and % Polymer		Final % Nortri-cyclene	Total Re-action Time In Hours	Remarks
109 g.	36	(33%)	63%	14	1.0% Catalyst at beginning 1.0% Catalyst replaced at 9 and 11 hours
180 g.	59	(33%)	63%	7	1.0% Catalyst at beginning 1.2% Catalyst replaced at 4 hours
139 g.	49	(35%)	74%	11	1.0% Catalyst at the beginning 1.1% Catalyst replaced at 8 hours
2688 g.	766	(29%)	63%	10	2% Catalyst at beginning 1.5% and 1.1% Catalyst replaced at 4 and 7.5 hours respectively
2431 g.	808	(33%)	64%	14	1.1% Catalyst at beginning 1.1% Catalyst replaced at 6, 8 and 12 hours
1880 g.	479	(26%)	63%	18	1.0% Catalyst at beginning 1.1% Catalyst replaced at 14.5 and 16 hours

a permanent violet colored reaction mixture is obtained. The re-
action mixture is then steam-distilled and 21.4 g. (60% yield) of
98% nortricyclene accompanied by 2% norbornene is isolated.

A large scale oxidation of equilibrated material was carried
out following the successful permanganate oxidation and removal of
norbornene on a small scale. The equilibrated mixture of nor-
bornene-nortricyclene after separation from polymer was added to
a 22 l. three necked flask containing 9 l. of water. A high speed
XP Lightnin stirrer equipped with a stainless steel, water cooled
graphite sealed stirrer agitated the reaction. A reflux condenser
was provided and the flask heated by immersing in an electrically
heated water bath. The bath is maintained at 65-68° which is ade-
quate to melt the hydrocarbon inside the flask. It is important
to keep the hydrocarbon molten in order to maintain good agita-
tion. Potassium permanganate is added in small portions at such
a rate as to maintain the reaction at 62-65°. Four moles of
potassium permanganate are added per mole of norbornene present
in isomerized mixture. After addition of this theoretical amount,
400-500 g. of additional potassium permanganate is added to insure
complete oxidation of norbornene. When the addition is complete,
the reaction mixture is stirred for 10-15 minutes, the reflux
condenser is replaced with a Vigreux column and splash head. The
splash head is connected to a condenser with warm water circu-
lating at 54-56°. The condenser is subsequently connected to a
three necked receiving flask containing ether which is cooled by
ice-cold water. A second condenser is connected to the three
necked receiving flask as an outlet for the system. The 22 l.

reaction flask is removed from the water-bath and heated with a 22 l. heating mantle. The nortricyclene was steam-distilled at 79° through the splash head and collected in the receiving flask as a solution in ether.

When all nortricyclene is distilled the temperature of the flask rises to about 99° and some water is collected in the receiving flask. The distillation is stopped, the ether containing the nortricyclene is separated from water layer, dried over anhydrous magnesium sulfate, filtered and the ether distilled through a Vigreux column. The nortricyclene is then distilled and collected as a solid (m.p. 56°) in the receiver. The recovered ether is used in subsequent runs. The last ether collection is distilled through a spiral column (30 cm. long and 3 turns per cm.) to remove ether from nortricyclene.

The results of several runs are given in Table V.

TABLE V

OXIDATION OF EQUILIBRATED MIXTURE WITH POTASSIUM PERMANGANATE

Weight Sample	% of Nortricyclene In Mixture	Grams KMnO₄ Added	Grams of Pure Nortricyclene Collected	% Yield
1050 g.	67	3225	621	88
936 g.	63	2770	514	87
715 g.	65	2400	404	87
990 g.	63	3200	531	85

An attempt was made to selectively oxidize norbornene in the presence of nortricyclene using ozone. However, it is difficult to prevent volatilization of nortricyclene by the oxygen stream and it is also difficult to separate nortricyclene from the methylene chloride used as reaction solvent. We also attempted oxidation of the mixture of norbornene and nortricyclene with chromium trioxide in acetic acid but found nortricyclene was also attacked. In view of these results permanganate oxidation appeared to be the reaction of choice.

IV. DISCUSSION

It has been shown that norbornene may be isomerized to a mixture of norbornene-nortricyclene using synthetic silica-alumina catalyst.

Three identical experiments using S-90, S-65, and S-46 were carried out to test the effectiveness of each catalyst. These results are shown in Table II and demonstrated that S-90 is the more efficient catalyst of this group. The maximum polymer formation was also observed with S-90 catalyst. However, the polymer yield could be reduced by reducing heating time.

Table III shows the results of isomerization experiments with 5% S-90 Houdry catalyst. These data show 71% of nortricyclene could be attained with 5% S-90 catalyst in three hours by heating at the reflux temperature. Additional heating increased the polymer yield rather than the yield of nortricyclene.

Table IV shows the effect of replacing the catalyst to provide fresh surface. This procedure gave an increase in nortricyclene at the expense of polymer. We found it advisable to change the S-90 catalyst frequently during a large scale reaction period. The factors necessitating catalyst change appeared to be the volume of norbornene and rate of reflux.

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Schleyer (15) conducted two experiments in which he obtained a mixture containing 71% nortricyclene with a single change of catalyst (1.1%). It has been our experience that these experimental conditions will not hold for large scale work and the maximum percentage of nortricyclene is 62-64% with 25-35% of accompanying polymer.

The data obtained from the oxidation of the isomerized norbornene-nortricyclene mixture is presented in Table V. The yield of nortricyclene is 86-88%. This does not include the partially oxidized material accumulating at top of the condenser. This material was collected and reoxidized as a separate step. The total yield of all products is 90-91%.

V. CONCLUSION

It has been demonstrated that norbornene may be isomerized to 62-64% of nortricyclene using Houdry S-90 catalyst. Pure nortricyclene may be obtained in 90% yield by selectively destroying norbornene in the norbornene-nortricyclene mixture with aqueous potassium permanganate.

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