spectrum of XII (Nujol mull) showed a maximum at 1698 cm.$^{-1}$ (C=O str.). The ultraviolet spectrum shows a phenanthrene nucleus with $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (ϵ 6.03 × 10^4).

2,3-Triphenylenedicarboxylic Anhydride (XIX).—A solution of 0.285 g. (0.943 mmole) of XI, 0.340 g. (1.91 mmoles) of N-bromosuccinimide and 15 mg. of benzoyl peroxide in 10 ml. of chloroform was heated at the reflux temperature for 12 hr. The mixture was cooled to 0° and 0.012 g. of light yellow crystals were collected, m.p. 338–345° subl. The mother liquor was heated with 20 ml. of 10% potassium hydroxide and filtered. The solution was acidified with concentrated hydrochloric acid to give a white precipitate. Two recrystallizations from diethyl phthalate followed by washing with benzene gave 0.090 g. (32%) of pure anhydride XIX, m.p. 349–350° subl.

Anal. Calcd. for $C_{20}H_{10}O_3$: C, 80.52; H, 3.37. Found: C, 80.21; H, 3.66.

The ultraviolet spectrum had the same general shape as triphenylene with $\lambda_{\max}^{\text{EtOH}}$ 266, 257 mμ (ϵ 6.20 and 4.82 × 10^4, respectively).

Triphenylene (XVIII).—A mixture of 0.25 g. (0.836 mmole) of XI and 30 ml. of 10% sodium hydroxide was heated until a clear solution was obtained. This solution was poured into a solution of 2.25 g. of potassium ferricyanide in 10 ml. of water and the solution heated at the reflux temperature for 24 hr., during which time a small amount of white needles had sublimed on the condensor walls. The mixture was cooled and the water solution was extracted with benzene. The combined benzene extracts were evaporated to dryness at reduced pressure to give 0.019 g. (9.7%) of triphenylene (XVIII), m.p. 190–195°, after one recrystallization from ethanol. The material showed no melting point depression when mixed with an authentic sample of triphenylene (Aldrich Chemical Co.). The ultraviolet spectrum was identical to the authentic sample.

1,2,5,6-Bis(9,10-phenanthro)cyclooctadiene (XXI). A. By Pyrolysis of Sulfone XVII in Diethyl Phthalate.—A solution of 0.700 g. (0.00265 mole) of XVII in 10 ml. of diethyl phthalate was heated at the boiling point until approximately half of the diethyl phthalate had distilled. The residue was cooled to room temperature and light yellow crystals precipitated. The crystals were washed with benzene to give 0.11 g. (20.9%) of XXI, m.p. 430–435° subl. The material was recrystallized from diethyl phthalate to give pure material, m.p. 438–440°. The melting point of a mixture of this sample and the sample obtained from the pyrolysis of acetate X was not depressed.

Addition of ethanol to the mother liquor gave material which melted over a range and appeared polymeric.

B. By Pyrolysis of Dimer XVI in Diethyl Phthalate.—A solution of 0.104 g. (0.254 mmole) of XVI, m.p. 228–229°, in 10 ml. of diethyl phthalate was heated at the boiling point until approximately half of the diethyl phthalate was distilled. The residue was cooled, and 0.032 g. (33%) of XXI, m.p. 430–438° subl., precipitated as a yellow powder. This product was shown to be the same as the hydrocarbon obtained from the pyrolysis of sulfone XVII and acetate X by comparison of the infrared and ultraviolet spectra and by the fact that the melting points of a mixture of these samples was undepressed.

Hydrolysis of the diethyl phthalate solution by stirring 2 days with 30% sodium hydroxide produced no crystalline products from the basic solution.

A similar result was obtained when the higher melting form of XVI was pyrolyzed under the same conditions. Attempts to trap the quinodimethane III as a possible intermediate in this rearrangement as the maleic anhydride adduct XI resulted only in the isolation of XXI.

Acknowledgment.—We wish to thank Dr. R. W. King and Dr. O. L. Chapman, Iowa State University, for the n.m.r. spectrum of XVI and for their helpful discussion as to the interpretation of the spectrum. We are grateful to Dr. R. W. Sauer, the Atlantic Refining Company, for mass spectrographic data on XXI.

Alumina: Catalyst and Support. XX.[1] Aromatization of n-Octane-4-C^{14} over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

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The aromatization of n-octane-4-C^{14} over chromia–alumina catalyst was investigated in order to demonstrate that cyclooctane adsorbed species participates in the aromatization reaction. Only a C_8-ring intermediate will lead to ethylbenzene having a labeled ethyl group in the α- and β-position. The present study provides evidence that at least 30% of the ethylbenzene produced at the beginning of the reaction proceeds *via* a 1,8-ring closure. The radioactivity distribution in the m- and p-xylene is in agreement with the proposed mechanism suggesting the participation of 1,7- and 1,8-ring in the transition state.

The aromatization of n-octane presents an interesting mechanistic problem. Herington and Rideal[3] reported the formation of ethylbenzene, and o-, m-, and p-xylene when n-octane was passed over chromia–alumina catalyst at elevated temperatures. Ethylbenzene and o-xylene could be explained by simple 1,6-ring closure, but this mechanism precludes the formation of m- and p-xylene. In order to account for their formation, Herington and Rideal proposed the formation of bicyclo[3.2.1]octane and bicyclo[2.2.2]-octane intermediates.

In studying the aromatization of n-octane-1-C^{14} over "nonacidic" chromia–alumina catalyst, Pines and Chen[4] have shown that no combination of mechanisms which contain the bicyclic intermediates of Herington and Rideal would fit their data. Pines and Chen explained their data by a combination of mechanisms involving 1,6-ring closure and the presence of 1,7- and 1,8- adsorbed species in the transition state.

The fact that methylcycloheptane has been isolated from the selectively hydrogenated reaction mixture from the aromatization of n-octane over "nonacidic" chromia–alumina catalyst[5] provides good evidence for the existence of a cycloheptane adsorbed species.

In order to demonstrate the existence of a cyclooctane adsorbed species, n-octane-4-C^{14} was synthesized and aromatized under conditions described previously.[6]

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[1] For paper XIX, see J. Herling and H. Pinesin, *Chem. Ind.* (London), 984 (1663).

[2] (a) Paper XI of the series "Aromatization of Hydrocarbons"; for paper X see S. M. Csicsery and H. Pines, *J. Am. Chem. Soc.*, **84**, 3939 (1962); (b) this research was supported by the U. S. Atomic Energy Commission, contract AT(11-1)-1046.

[3] E. F. G. Herington and E. R. Rideal, *Proc. Roy. Soc.*, **184A**, 434, 447 (1945).

[4] Proceedings from the Second International Congress in Catalysis, Paris, 1960, pp. 367–387, edited by TECHNIP, Paris, 1961.

[5] S. M. Csicsery, Ph.D. thesis, "Contribution to the Mechanism of Dehydrogenation, Dehydrocyclization and Dehydroisomerization of Hydrocarbons over Chromia–Alumina Catalysis," Northwestern University (1962), Table XLVIII.

[6] H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962).

CHART I
AROMATIZATION OF n-OCTANE-4-C^{14} THROUGH CYCLOOCTANE ADSORBED SPECIES

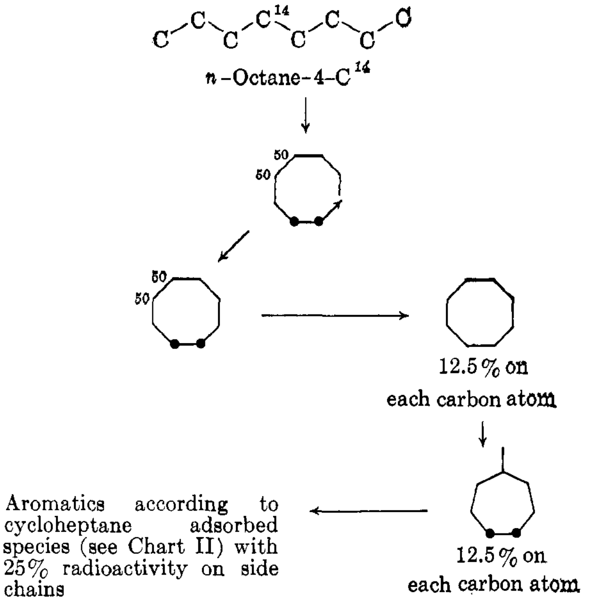
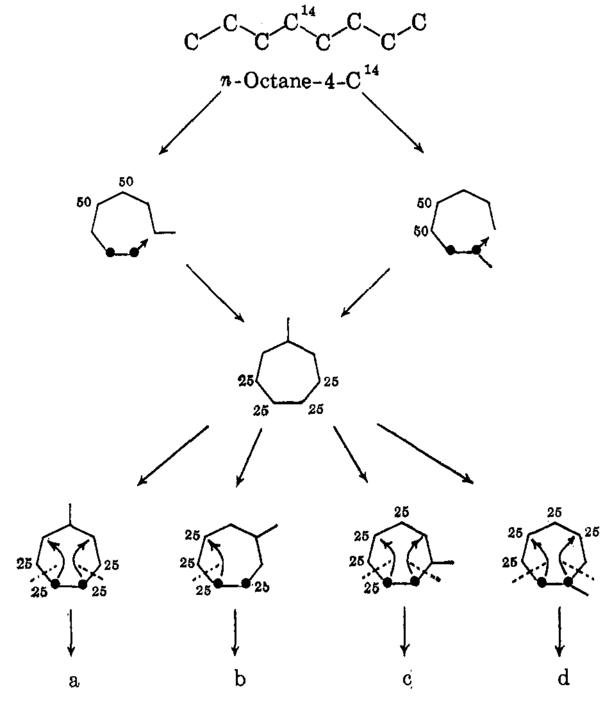


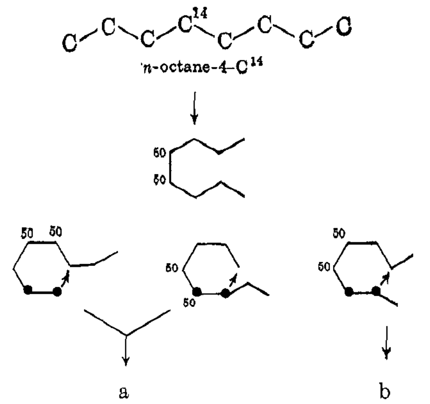
CHART II
AROMATIZATION OF n-OCTANE-4-C^{14} THROUGH CYCLOHEPTANE ADSORBED SPECIES



a, o-Xylene 25% on side chain
b, m-Xylene 25% on side chain
c, p-Xylene 25% on side chain; ethylbenzene 0% on side chain
d, m-Xylene 25% on side chain; o-xylene 0% on side chain

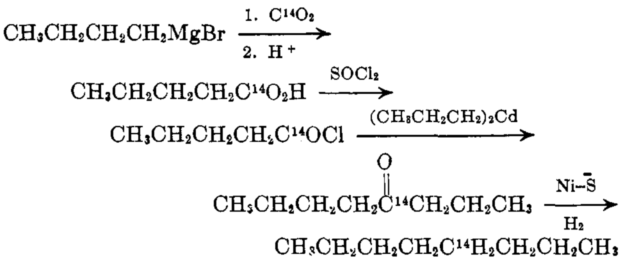
The experimental data described previously[4] led to the conclusion that the carbon atoms, in the mechanism involving a cyclooctane adsorbed species, acquire isotopic equivalency by "rolling around" on the catalyst. The xylenes and ethylbenzene obtained from n-octane-4-C^{14} *via* cyclooctane must have, therefore, 25% of radioactivity in the side chain (Chart I). A cycloheptane adsorbed species would predict side-chain labels of 25% for m- and p-xylene, 0–25% for o-xylene, and 0% for ethylbenzene (Chart II), while 1:6-closure would predict side-chain labels of 0% for the o-xylene and ethylbenzene produced (Chart III).[7a,b] Therefore, the existence of any side-chain label in ethylbenzene would be a direct indication of a cyclooctane adsorbed species, since ethylbenzene could not acquire side chain label by any of the other mechanisms. Furthermore the side-chain label in ethylbenzene should be equally distributed between α and β carbon atoms.

CHART III
AROMATIZATION OF n-OCTANE-4-C^{14} THROUGH 1:6-CLOSURE



a, Ethylbenzene 0% on side chain
b, o-Xylene 0% on side chain

Procedure.—The n-octane-4-C^{14} was synthesized in 98.2% purity and 11% over-all yield by the following sequence of reactions.



$$CH_3CH_2CH_2CH_2MgBr \xrightarrow[2.\ H^+]{1.\ C^{14}O_2}$$
$$CH_3CH_2CH_2CH_2C^{14}O_2H \xrightarrow{SOCl_2}$$
$$CH_3CH_2CH_2CH_2C^{14}OCl \xrightarrow{(CH_3CH_2CH_2)_2Cd}$$
$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C^{14}}CH_2CH_2CH_3 \xrightarrow[H_2]{Ni-\bar{S}}$$
$$CH_3CH_2CH_2CH_2C^{14}H_2CH_2CH_2CH_3$$

The n-octane-4-C^{14} was dehydrogenated at 522° over "nonacidic" chromia–alumina catalyst by a previously described procedure.[6] Table I summarizes the reaction conditions and composition of the aromatic fraction.

The reaction product was collected in three almost equal cuts. Each cut was separated by preparative v.p.c. Three different fractions were collected; the first containing the nonaromatics and toluene, the second composed of ethylbenzene, m- and p-xylene, and the third fraction containing o-xylene. The second and third fractions were diluted with their corresponding inactive aromatic compounds and oxidized with alkaline potassium permanganate to their respective acids. The aromatic acids were then separated by the procedure described previously.[7b]

The benzoic, isophthalic, and terephthalic acids were decarboxylated in boiling quinoline with copper oxide and the benzene and carbon dioxide products analyzed

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(7) (a) The exact attachment of the hydrocarbon to the catalyst in charts I–III is purely for illustrative purposes. Although the hydrocarbon must be adsorbed on the catalyst before any reaction will occur, the attachment may be other then that indicated. (b) H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

TABLE I

AROMATIZATION OF n-OCTANE-4-C^{14} OVER CHROMIA–ALUMINA CATALYST[a]

Cut	1	2	3
Length of cuts, min.	11.0	11.0	12.4
Total C_8H_{18} passed, ml.	3.5	3.5	3.8
Liquid product recovered, g.	2.00	2.33	2.47
C_8H_{18} converted to aromatics, mole %	10.9	9.8	9.9
C_8H_{18} converted to carbonaceous[b] material, mole %	←0.31→		
Composition of aromatic fraction, mole %			
Toluene	10.1	11.1	10.3
Ethylbenzene	27.4	24.7	29.5
o-Xylene	35.5	43.8	45.3
m-Xylene	16.2	15.3	10.1
p-Xylene	10.8	5.1	4.8

[a] The experiment was made at 522° and at an hourly liquid space velocity of 1.38. [b] The conversion to carbonaceous material was determined at the end of the experiment.

for radioactivity. The Schmidt reaction was employed for decarboxylation of the phthalic acid, carbon dioxide and anthranilic acid being the products. Tables II and III summarize the radioactivities of the aromatic acids and their decarboxylation products. The differences between the radioactivity of the acids and the total radioactivity of their decarboxylation was less than ±3%.

TABLE III

RADIOCHEMICAL ASSAY DATA

Schmidt reaction on phthalic acid derived from o-xylene produced by the aromatization of n-octane-4-C^{14}

Cut	1	2	3
Phthalic acid decarboxylated, mmoles	6.03	6.03	6.03
Barium carbonate obtained, mmoles	5.30	2.24	2.65
Anthranilic acid obtained, mmoles	0.13	0.75	1.33
Barium carbonate yield, mole %	88	37	44
Anthranilic acid yield, mole %	2.2	11	22
Radioactivities, 10^{-3} μc./mmole.			
Phthalic acid	73	188	170
Barium carbonate	1.4	2.2	1.82
Anthranilic acid	72.5	181	163

Discussion of Results

The radioactivity distribution of the product from the aromatization of n-octane-4-C^{14} over "nonacidic" chromia–alumina catalyst is summarized in Table IV.

The fact that ethylbenzene has radioactivity in the side chain proves the existence of a cyclooctane adsorbed species.

The time-dependent dehydrocyclization, previously discussed[4,8–10], was confirmed by present results. The side-chain label for ethylbenzene from 7.8% to 5.0% for cuts 1–3, respectively, corresponds to a drop of 31% to 20% for the contribution of the cyclooctane adsorbed species. The fact that the formation of ethylbenzene initially drops and then begins to increase suggests that the catalytic sites for cyclooctane adsorption diminish more rapidly than cycloheptane adsorption or that 1:6-closure increases.

The radioactivity distribution of the m- and p-xylenes corresponds to the predicted 25% side-chain and 75% ring labels. This is in agreement with cycloheptane and cyclooctane adsorbed species during their formation. If m- and p-xylene would have been produced from the isomerization of o-xylene, their side chain labels would have been much lower. This observation is in agreement with previous results.[9]

TABLE II

DECARBOXYLATIONS OF ACIDS DERIVED FROM ETHYLBENZENE, p-XYLENE, AND m-XYLENE PRODUCED BY THE AROMATIZATION OF n-OCTANE-4-C^{14}

	Ethylbenzene			p-Xylene			m-Xylene		
Cut	1	2	3	1	2	3	1	2	3
Acid decarboxylated,[a] mmole	1.68	2.07	2.42	1.15	1.59	1.24	1.27	1.41	1.41
Barium carbonate obtained, mmoles	1.58	1.88	2.32	2.01	3.02	2.16	2.20	2.54	2.68
Benzene obtained, mmoles	0.26	0.58	0.63	0.30	0.51	0.32	0.17	0.38	0.42
Barium carbonate yield, mole %	94	91	96	87	95	87	87	90	95
Benzene yield, mole %	15	28	26	26	32	26	13	27	30
Radioactivities, 10^{-3} μc./mmole									
Starting acid[a]	59.2	161	250	65.3	70.6	67.2	40.8	259	239
Barium carbonate	2.3	5.5	6.2	6.8	8.1	7.7	4.2	27.2	25.6
Benzene	56.7	156	242	49.2	52.3	50.6	31.5	197	182

[a] For ethylbenzene, benzoic acid; for p-xylene, terephthalic acid; for m-xylene, isophthalic acid.

Using previous data[4] for the aromatization of n-octane-1-C^{14} over chromia–alumina-B, it can be shown that cycloheptane and cyclooctane adsorbed species each contribute 50% to the initial formation of m- and p-xylene.

Since only cyclooctane and cycloheptane adsorbed species contribute to the formation of m- and p-xylene, and the cyclooctane adsorbed species diminishes with time, the amount of m- and p-xylene produced should also diminish with time. This is substantiated as seen in the drop of m-xylene formed from 16.2% to 10.1% and that of p-xylene from 10.8% to 4.8% (cuts 1–3, Table I).

The very low side-chain radioactivity in o-xylene shows that mostly 1:6-ring closure operated during its formation.

Conclusion

The present study has proved the existence of a cyclooctane adsorbed species as one of the intermediates for the aromatization of n-octane over chromia–alumina catalyst. It has also been shown that 1,8-ring formation decreases with time.

The formation of m- and p-xylene is *via* cycloheptane and cyclooctane adsorbed species with none or very little arising from the isomerization of o-xylene. However, the contribution of large ring intermediates for

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(8) C. T. Chen, W. O. Haag and H. Pines, *Chem. Ind.* (London), 1379 (1959).

(9) H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

(10) H. Pines and C. T. Chen, *J. Org. Chem.*, **26**, 1057 (1961).

TABLE IV

RADIOACTIVITY DISTRIBUTION FROM THE AROMATIZATION OF n-OCTANE-4-C^{14} OVER NONACIDIC CHROMIA–ALUMINA CATALYST

	Cut 1			Cut 2			Cut 3		
	Ring, %	Side chain, %	Difference,[a] %	Ring, %	Side chain, %	Difference,[a] %	Ring, %	Side chain, %	Difference,[a] %
Ethylbenzene	91.5	7.8	−0.7	95.4	6.8	+2.2	94.3	5.0	−0.7
o-Xylene	96.8	3.9	+0.7	95.0	2.3	−2.7	95.0	2.1	−2.9
m-Xylene	77.4	20.4	−2.2	76.2	21.0	−2.8	76.2	21.4	−2.4
p-Xylene	75.4	21.2	−3.4	74.2	23.0	−2.8	75.3	23.0	−1.7

[a] Difference between the experimental value and 100% radioactivity recovery.

o-xylene formation is small with 1:6-closure being the major contributor.

Experimental

n-Octane-4-C^{14}. A. Valeric Acid 1-C^{14}.—To 3.9 g. (0.024 mole) of n-butylmagnesium bromide was added 0.87 g. (0.020 mole) of radioactive carbon dioxide (radioactivity, 10 mc.) according to a procedure already described.[11] The acid was converted to valeryl chloride with thionyl chloride in benzene solution.

B. 4-Octanone-4-C^{14}.—The following procedure for making and using di-n-propylcadmium was taken from the general procedure described by Cason.[12]

To a refluxing stirred solution of a Grignard reagent made from 6.3 g. (0.26 g.-atom) of magnesium and 31.3 g. (0.25 mole) of 1-bromopropane in 300 ml. of dry ether was added, under nitrogen, 21.4 g. (0.117 mole) of dry cadmium chloride over a 10-min. period. After an hour of refluxing, the ether was removed *in vacuo*. To remove the last traces of ether two 140-ml. portions of benzene were added and removed by distillation *in vacuo*. Finally 200 ml. of dry benzene was added to the solid mixture of di-n-propylcadmium and magnesium salts. The valeryl chloride-1-C^{14} was then added, and after 1.5 hr. of refluxing, the reaction mixture was poured onto ice, 115 ml. of 10% sulfuric acid was added, and aqueous and organic layers were separated. The aqueous layer was extracted several times with ether. The organic layer was washed with dilute potassium carbonate and water. The combined organic layers were dried over magnesium sulfate. The ether and most of the benzene were removed by distillation. The residue, 21.8 g., contained 14.2 g. of 4-octanone. The semicarbazone of a similarly prepared inactive 4-octanone melted at 97° (lit.[13] m.p. 96°).

C. n-Octane-4-C^{14}.—The foregoing residue was hydrogenolyzed in a 125-ml. rotating autoclave at 277° over 1.508 g. of nickel–kieselguhr catalyst (66.6 wt. % Ni) modified by 0.35 g. of thiophene.[14] The starting hydrogen pressure was 128 atm.; the highest pressure at 268° was 258 atm. The autoclave was rinsed with inactive n-octane, which was later added to the reaction product. The n-octane diluted with n-pentane was chromatographed through a 160-cm. column filled with 60/200-mesh "950" Davison Silica-Gel, and distilled through a 30-cm. Vigreux column. The main fraction weighed 32 g. The purity was 98.2% with an 11% yield based on BaC^{14}O$_3$ used; radioactivity, 3.9 μc. per mmole of n-octane.

Catalyst.—The chromia–alumina catalyst was prepared according to the procedure described previously.[9] The alumina was precipitated from sodium aluminate and impregnated with chromic acid. The catalyst contained 13.8 wt. % of Cr_2O_3, its surface area was 89 m.^{2}/g., and average pellet weight was 0.022 g.

Apparatus and Procedure.—The apparatus and procedure were the same as described in previous publications.[6]

Separation of Aromatic Hydrocarbons from the Aromatization of n-Octane-C^{14}.—The separation was done using a F & M Model 300 programmed temperature gas chromatograph (15) with an 11 mm. × 2.4 m. preparative v.p.c. column filled with 5% 7,8-benzoquinoline on 30–60-mesh Chromosorb. The temperature used was 80° at 150 ml./min. helium flow rate. Sample injection sizes were from 0.8–1.2 ml. The sample recovery procedure was the same as that described previously.[6] Three fractions were taken: (1) nonaromatics and toluene, (2) ethylbenzene, m- and p-xylene, and (3) o-xylene. Fractions 2 and 3 were diluted with inactive hydrocarbons before oxidation.

Oxidation of Aromatics.—These diluted fractions 2 and 3 were oxidized separately with hot alkaline potassium permanganate to the corresponding acids. The oxidation was accomplished by rapidly stirring, at 100° for 18 hr., 12.0 g. (0.085 mole) of potassium permanganate in 250 ml. of water containing 15 drops of 5% sodium hydroxide and the aromatic fraction. At the end of this time, 4.0 ml. of methyl alcohol was added and heating and stirring continued for 0.5 hr. The salts were removed by suction filtration and washed with about 300 ml. of water. At this point, oxidized fraction 2 was diluted to *ca.* 1000 ml., then acidified with 10 ml. of concentrated hydrochloric acid. Oxidized fraction 3 was evaporated on a hot plate to about 125 ml. then acidified with 5 ml. of concentrated hydrochloric acid.

Separation of Aromatic Acids.—The benzoic, isophthalic, and terephthalic acids formed from the oxidation of fraction 2 were separated by a procedure described previously.[7] Purification of the phthalic acid formed from the oxidation of fraction 3 was accomplished as described previously.[7]

Radiochemical Assay.—The radiochemical assay of the resulting aromatic acids and of their decarboxylation products was made according to the procedure reported previously.[16]

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[11] C. T. Chen, Doctoral dissertation, Northwestern University, 1959, p. 31.

[12] J. Cason, *Chem. Rev.*, **40**, 15 (1957).

[13] L. Bouveault and R. Locquin, *Bull. soc. chim. France*, (3) **35**, 629 1906).

[14] H. Pines, M. Shamaiengar, and W. S. Postl, *J. Am. Chem. Soc.*, **77**, 5099 (1955).

[15] F & M Scientific Corp., New Castle, Del.

[16] H. Pines and G. Benoy, *J. Am. Chem. Soc.*, **82**, 2483 (1960).