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A Destructive Ethylation Reaction of Benzene with 3-Methylpentane-1-^{14}C

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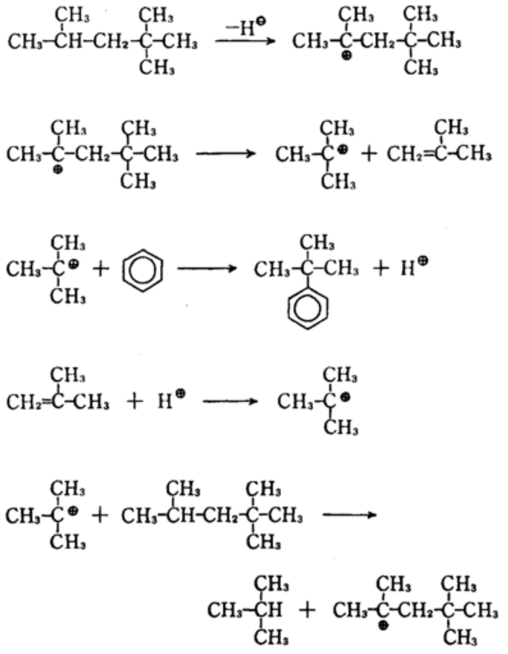
The destructive alkylation reaction of benzene with 3-methylpentane to give ethylbenzene in the presence of aluminum chloride was investigated. When 3-methylpentane-1-^{14}C was employed, radioactive ethylbenzene was obtained. A radioassay of radioactive ethylbenzene showed that: a) the specific radioactivity of the ethylbenzene was about one-third that of the starting 3-methylpentane-1-^{14}C, and b) more than 90% of the radioactivity of the ethylbenzene was present on the β-carbon atom of the ethyl group. These findings suggested a preceding equilibrium between 3-methylpentane and 2-methylpentane, which resulted in an equivalent localization of the radioactive label on three methyl groups of these C_6-hydrocarbons. A carbonium-ion mechanism including an intermediate ethyl cation was discussed in detail.

In 1935, Ipatieff and his co-workers[1–3] reported that the treatment of benzene with 2,2,4-trimethylpentane in the presence of an aluminum chloride-hydrogen chloride catalyst yielded *t*-butylbenzene and p-di-*t*-butylbenzene as well as isobutane. This method of preparing alkylbenzenes from arenes and alkanes was found to be affected by many kinds of Friedel-Crafts catalysts.

These reactions, examples of what Ipatieff originally termed “Destructive Alkylation,”[4] probably proceed through a carbonium-ion process. A scheme for the *t*-butylbenzene formation may be represented as is shown. The scheme involves: 1) hydride abstraction from 2,2,4-trimethylpentane by an appropriate catalytic species to give a tertiary cation, 2) which then affords a *t*-butyl cation and an isobutene molecule by β-cleavage reaction. 3) The *t*-butyl cation formed by the β-cleavage and/or formed from isobutene by the addition of a proton, alkylates benzene to give *t*-butylbenzene. 4) The *t*-butyl cation can abstract the hydride ion from 2,2,4-trimethylpentane to give isobutane and the tertiary cation.



In the destructive alkylation of the C_6-alkanes-benzene system, ethylbenzene has been reported to be the main product. Actually, in the presence of an aluminum chloride-hydrogen chloride catalyst, the destructive alkylation of benzene with 3-methylpentane afforded ethylbenzene and a small amount of an alkylbenzene mixture.[5] Most probably, the attacking species in the formation of ethylbenzene is either ethylene or ethyl cation; however, the mode of the cleavage of 3-methylpentane remains to be examined.

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[1] A. V. Grosse and V. N. Ipatieff, *J. Am. Chem. Soc.*, **57**, 2415 (1935).

[2] V. N. Ipatieff, V. I. Komarewsky and H. Pines, *ibid.*, **58**, 918 (1936).

[3] A. V. Grosse, J. M. Mavity and V. N. Ipatieff, *J. Org. Chem.*, **3**, 137, 448 (1938).

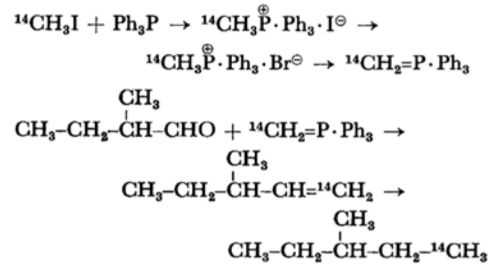
[4] For discussions of this and related reactions, see S. H. Patinkin and B. S. Friedman, “Friedel-Crafts and Related Reactions,” edited by G. A. Olah, Vol. II, Interscience Publishers, New York, (1964), p. 110.

[5] T. Hatsui, M. Sc. Thesis (Kyoto University, 1967).

In the present paper, the authors wish to present some experimental results which may shed light on the mechanism of the formation of ethylbenzene in a "destructive alkylation" reaction. A tracer experiment was performed using 3-methylpentane-1-^{14}C.

Results

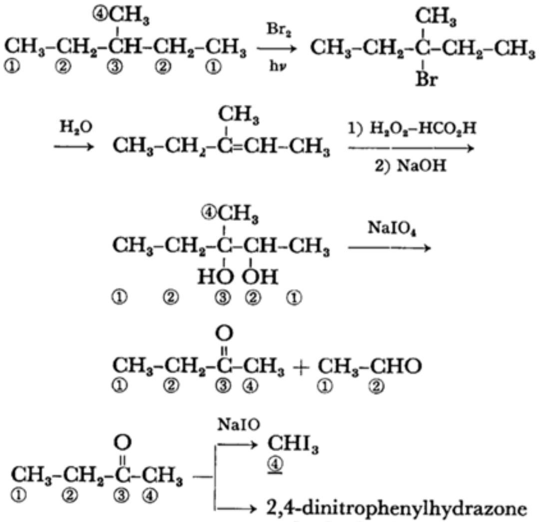
Synthesis and Degradation of 3-Methylpentane-1-^{14}C. Carbon-14-labeled 3-methylpentane was prepared in the following way:



$$^{14}CH_3I + Ph_3P \rightarrow {}^{14}CH_3\overset{\oplus}{P}\cdot Ph_3\cdot I^{\ominus} \rightarrow {}^{14}CH_3\overset{\oplus}{P}\cdot Ph_3\cdot Br^{\ominus} \rightarrow {}^{14}CH_2{=}P\cdot Ph_3$$

$$CH_3–CH_2–\overset{CH_3}{CH}–CHO + {}^{14}CH_2{=}P\cdot Ph_3 \rightarrow CH_3–CH_2–\overset{CH_3}{CH}–CH{=}{}^{14}CH_2 \rightarrow CH_3–CH_2–\overset{CH_3}{CH}–CH_2–{}^{14}CH_3$$

The Wittig reaction of 2-methylbutanal with methyltriphenylphosphonium bromide-methyl-^{14}C, followed by a catalytic hydrogenation, gave 3-methylpentane-1-^{14}C (5.28 μCi/mol).[*2] A carrier was used where necessary. The systematic degradation of this labeled hydrocarbon was carried out as follows:



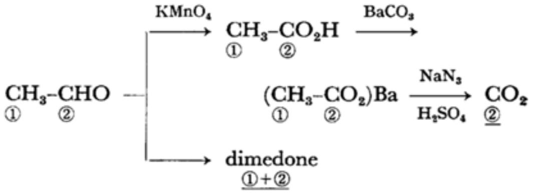
$$\underset{①}{CH_3}–\underset{②}{CH_2}–\underset{③}{\overset{④CH_3}{CH}}–\underset{②}{CH_2}–\underset{①}{CH_3} \xrightarrow[h\nu]{Br_2} CH_3–CH_2–\underset{Br}{\overset{CH_3}{C}}–CH_2–CH_3$$

$$\xrightarrow{H_2O} CH_3–CH_2–\overset{CH_3}{C}{=}CH–CH_3 \xrightarrow[2)\ NaOH]{1)\ H_2O_2–HCO_2H}$$

$$\underset{①}{CH_3}–\underset{②}{CH_2}–\underset{③}{\underset{HO}{\overset{④CH_3}{C}}}–\underset{②}{\underset{OH}{CH}}–\underset{①}{CH_3} \xrightarrow{NaIO_4}$$

$$\underset{①}{CH_3}–\underset{②}{CH_2}–\underset{③}{\overset{O}{\overset{\|}{C}}}–\underset{④}{CH_3} + \underset{①}{CH_3}–\underset{②}{CHO}$$

$$\underset{①}{CH_3}–\underset{②}{CH_2}–\underset{③}{\overset{O}{\overset{\|}{C}}}–\underset{④}{CH_3} \begin{cases}\xrightarrow{NaIO} \underset{\underline{④}}{CHI_3}\\ \longrightarrow \underset{\underline{①+②+③+④}}{\text{2,4-dinitrophenylhydrazone}}\end{cases}$$



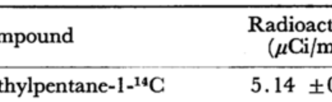
$$\underset{①\ \ \ ②}{CH_3–CHO} \begin{cases}\xrightarrow{KMnO_4} \underset{①\ \ \ ②}{CH_3–CO_2H} \xrightarrow{BaCO_3} \underset{①\ \ \ ②}{(CH_3–CO_2)Ba} \xrightarrow[H_2SO_4]{NaN_3} \underset{\underline{②}}{CO_2}\\ \longrightarrow \underset{\underline{①+②}}{\text{dimedone}}\end{cases}$$

All the processes used were standard methods and were known to proceed without skeletal rearrangements. The results obtained (Table 1) show all the radioactivity was present on C-1.

TABLE 1. RADIOASSAY OF ^{14}C-LABELED 3-METHYLPENTANE

Compound	Radioactivity (μCi/mol)
3-Methylpentane	1.12 ±0.05
Acetaldehyde dimedone	1.12 ±0.05
$BaCO_3$	0.0122±0.0006
Iodoform	0.0195±0.0004
Methyl ethyl ketone 2,4-dinitrophenylhydrazone	1.16 ±0.05

Destructive Alkylation. Preliminary experiments[5] showed that the products of the destructive alkylation of benzene with 3-methylpentane under the influence of aluminum chloride at an elevated temperature were mainly ethylbenzene and isobutane. Small amounts of toluene and xylenes were also formed, besides a trace amount of *t*-butylbenzene. 3-Methylpentane and 2-methylpentane (a rearranged hydrocarbon) were also recovered. In a tracer experiment, therefore, 3-methylpentane-1-^{14}C was placed in the same conditions. At a relatively low conversion, ethylbenzene was collected by a preparative g. l. c.; it was found to be radioactive. Radioactive ethylbenzene was degraded as follows:



The results of radioassay are shown in Table 2. Table 2 shows that 93% of radioactivity was present on the β-carbon atom of ethylbenzene.

TABLE 2. RADIOASSAY OF ^{14}C-LABELED ETHYLBENZENE

Compound	Radioactivity* (μCi/mol)
3-Methylpentane-1-^{14}C	5.14 ±0.03
Ethylbenzene	1.53 ±0.01
Benzoic acid	0.106±0.001

* The probable error was less than 2%.

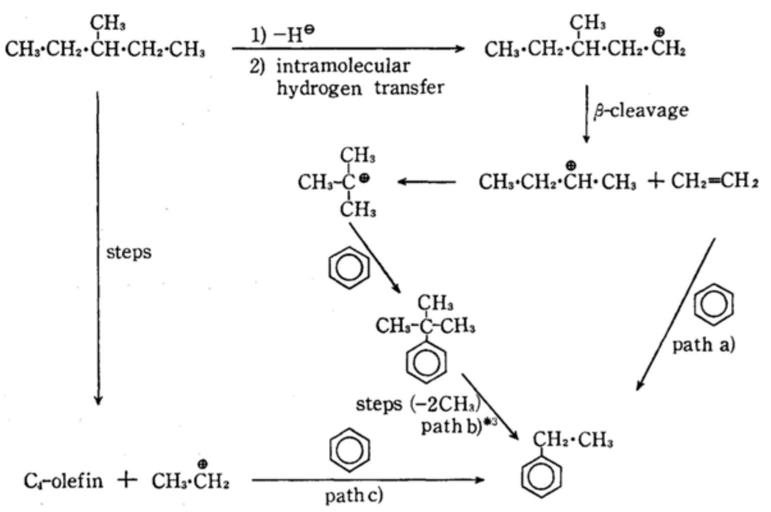
Discussion

The results of the tracer experiment (Table 2)

[*2] The Wittig reaction of pentanone-3 with methyltriphenylphosphonium bromide-methyl-^{14}C, followed by hydrogenation, gave 3-methylpentane-3-methyl-^{14}C in an improved yield (overall, 65%). An improbable but still conceivable idea of compelxity due to a slow isomerization to 2-methylpentane made the authors hesitate to use this labeled hydrocarbon. The present results show the rapid interconversion of methylpentanes during the "destructive alkylation" and, consequently, show the usefulness of 3-methylpentane-3-methyl-^{14}C.

show the important features of the "destructive ethylation" reaction. The oxidation of radioactive ethylbenzene to benzoic acid reveals that more than 90% of the radioactivity was present on the β-carbon atom of ethylbenzene. Although the origin of the radioactivity on the α-carbon atom (less than 10%) remains uncertain, this result clearly shows that no symmetric C_2-compound could be an intermediate of the reaction. Mention should be made of the specific activity of the product, ethylbenzene. The observed figure (1.53 μCi/mol) was very close to one-third of the activity of the starting material, 3-methylpentane (5.14 μCi/mol). Any mechanism that can be applicable in the present investigation should be able to give a rational explanation of the above findings.

Three pathways can be postulated for the formation of ethylbenzene in the destructive alkylation. They are: a) the reaction of ethylene with benzene; b) the formation of *t*-butylbenzene or higher alkylbenzenes by the reaction of *t*-butyl or other higher alkyl cations with benzene, followed by a sidechain demethylation to give ethylbenzene, and c) the reaction of the ethyl cation with benzene. These are summarized in the following scheme:



The results of the tracer experiment eliminate path a), the intervention of ethylene or other symmetric C_2-species as a direct precursor of ethylbenzene. Symmetrical intermediate(s) should incorporate an equal amount of radioactivity on both the α- and β-carbon atoms of ethylbenzene; however, this was found not to be the case.

Path b) can be ruled out by examining the fate of *t*-butylbenzene under the destructive alkylation conditions. The treatment of *t*-butylbenzene in benzene with aluminum chloride at an elevated temperature afforded not only ethylbenzene, but in addition, cumene, toluene, and *n*-propylbenzene. These four products were found to be produced in comparable amounts. One of the important features is that an appreciable amount of *t*-butylbenzene survived even after a considerable amount of alkylbenzenes had been formed. In the present instance of a destructive ethylation reaction, the ethylbenzene formed was accompanied by only small amounts of cumene and *n*-propylbenzene and by only a trace of *t*-butylbenzene. These findings suggest that the *t*-butylbenzene route (or path b) can not constitute a major part of the ethylbenzene formation under the conditions used.

Path c) remains to be examined. The intervention of the ethyl cation in the Friedel-Crafts reaction with ethyl halides is a well-known phenomenon. Roberts, Ropp, and Neville[6] reported that the reaction of ethyl-β-^{14}C chloride with benzene in the presence of aluminum chloride gave ethyl-β-^{14}C-benzene. They also found that ethyl-β-^{14}C-benzene showed little or no tendency to randomize its radioactivity even under vigorous Friedel-Crafts conditions. The results in Table 2 strongly suggest that the attacking species is the ethyl cation;[*4] that is, path c) might be followed.

A reasonable explanation of the specific radioactivity of ethylbenzene may be given in terms of a

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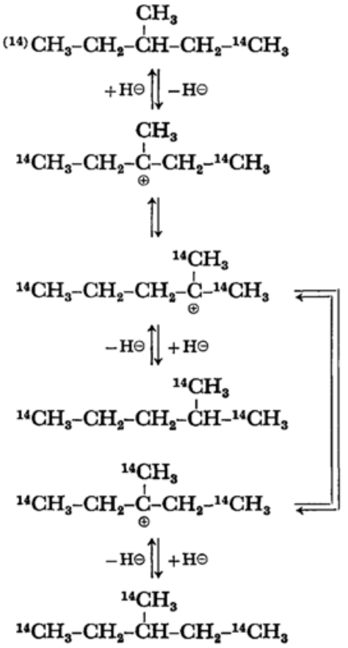
[*3] Or *via* higher alkylated benzene(s).

6) R. M. Roberts, G. A. Ropp and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 1764 (1955).

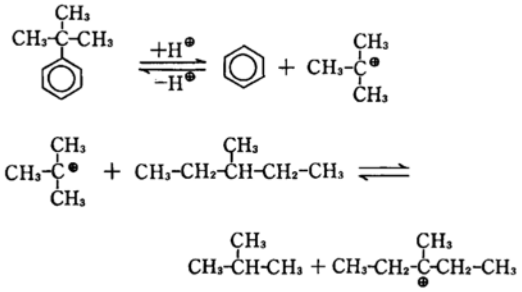
[*4] The ethyl cation may be in a form of an aluminum chloride complex or in a tight ion pair. Interventions of the carbonium ion intermediates are thoroughly discussed in the leading references. For a detailed discussions, *cf.* G. A. Olah and M. W. Meyer, "Friedel-Crafts and Related Reactions," edited by G. A. Olah, Vol. I, Interscience Publishers, New York (1963), p. 623.

rapid equilibrium between 3-methylpentane and 2-methylpentane in the presence of aluminum chloride. Schneider and Kennedy[7] have reported an isomerization of 3-methylpentane to 2-methylpentane, and *vice versa*, catalysed by Friedel-Crafts catalysts. Evering and Waugh[8] have presented the rate constants of an aluminum chloride-catalyzed isomerization reaction. The rate constants in *n*-hexane at 100°C were 150 hr^{-1} and 65 hr^{-1} for the isomerization of 3-methylpentane to 2-methylpentane, and for the reverse reaction, respectively. In addition, Karabatsos *et al.*[9] proved that there was no mixing between terminal carbon atoms and internal carbon atoms during the isomerizations of saturated hydrocarbons under the influence of the Friedel-Crafts catalysts. A rapid interconversion of this sort gives rise to radioactive randomization; hence, the three terminal methyl groups in 2- and 3-methylpentanes become equally labeled by radioactive carbon atoms, as is shown in the following scheme:



These equilibria indicate the presence of the 1,1-dimethylbutyl cation (and its conjugate acid, 2-methylpentane) in the reaction mixture. From the well-known β-cleavage rule, the precursor of the ethyl cation should be the 1,1-dimethylbutyl cation rather than the 1-methyl-1-ethylpropyl cation. The β-cleavage process now gives rise to the ethyl cation and isobutene. The presence of isobutane as the main product in the destructive alkylation of 3-methylpentane instead of isobutene shows another feature of the reaction. Isobutene can be converted into *t*-butylbenzene in the presence of benzene under Friedel-Crafts alkylation conditions. Surprisingly, in the present investigation, essentially no *t*-butylbenzene was isolated from the reaction mixture. It seemed of interest to determine the fate of *t*-butylbenzene.

In a destructive alkylation in the presence of added *t*-butylbenzene, g. l. c. analysis showed the rapid disappearance of *t*-butylbenzene, and the formation of a large amount of isobutane. The amount of ethylbenzene produced was not substantially affected by the addition of *t*-butylbenzene. From these observations, the following scheme may be suggested for the fate of *t*-butylbenzene under the present conditions:



From the experimental results and from the considerations cited above, one can postulate the following reaction scheme for the destructive ethylation of benzene with 3-methylpentane in the presence of aluminum chloride at an elevated temperature. The first stage of the reaction is the initiation of the reaction by an abstraction of hydride from 3-methylpentane with a polarized catalyst complex to give the tertiary cation. The cation produced is involved in a rapid equilibrium with a tertiary cation from 2-methylpentane, which is subjected to the β-cleavage reaction to yield an ethyl cation and isobutene. The ethyl cation thus formed alkylates benzene to give ethylbenzene, and isobutene is protonated to give the *t*-butyl cation. The role of the *t*-butyl cation is either to alkylate benzene to give *t*-butylbenzene, or to abstract hydride from 3-methylpentane (or 2-methylpentane as well) to give the carbonium ion. The last sequence of the reaction would maintain the reaction cycle.

Experimental

All the melting and boiling points are uncorrected. Glc analyses were carried out by means of a Yanagimoto Gas Chromatograph G.C.G.-5DH with 5% TG-3000 on a Celite 545 (40—60 mesh) 2.25-m column, and preparative glc was achieved using Yanagimoto G.C.G.-2 with a silicon-grease DC-703 2-m column.

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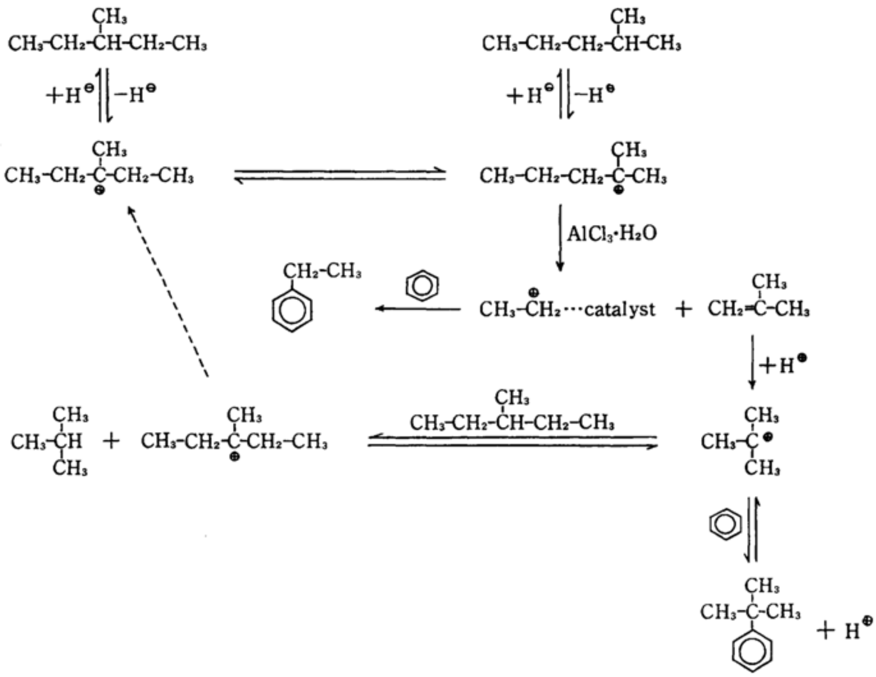
7) A. Schneider and R. M. Kennedy, *J. Am. Chem. Soc.*, **73**, 5013, 5017, 5024 (1951).

8) B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

9) G. J. Karabatsos *et al.*, *J. Am. Chem. Soc.*, **85**, 729, 733 (1963).



Radioactivity Assay. The radioactivity was measured by means of a Nuclear Chicago Liquid Scintillation Spectrometer 6801, using dioxane-base organic phosphor (1,4-dioxane : naphthalene : POP : POPOP=1 *l* : 120g: 7g : 0.05 g). Correction was made for the quenching using 3-methylpentane-^{14}C as the internal standard. Methyl ethyl ketone 2,4-dinitrophenylhydrazone and iodoform were converted into carbon dioxide in a Barker-type wet-combustion apparatus; carbon dioxide fixed with ethanolamine was served for assay.

Preparation of Methyltriphenylphosphonium Bromide-methyl-^{14}C. In a vacum manifold, methyl iodide-^{14}C (100 μCi, from the Radiochemical Center, Amersham) was transferred on 10-fold equivalents of triphenylphosphine by the aid of liquid nitrogen. The mixture was then warmed to 30°C and chilled again. This procedure was repeated several times, and the total system was flushed with non-radioactive methyl iodide. The methyl iodide washing was condensed on triphenylphosphine to give essentially quantitative yield of methyltriphenylphosphonium iodide-methyl-^{14}C. The crude iodide was dissolved in aqueous ethanol and was treated with freshly-prepared silver oxide. The mixture was filtered, and the precipitate was treated with non-active methyltriphenylphosphonium iodide several times. The combined filtrate and washings was acidified with hydrobromic acid, and the solution was concentrated to dryness. The residue was recrystallized from ethanol-ether to give pure methyltriphenylphosphonium bromide-methyl-^{14}C in a radioactive yield of over 90%.

Preparation of 3-Methylpentane-1-^{14}C. In a 15-m*l* centrifugal tube stoppered with a serum cap, was placed 0.26 g of sodium hydride (53% mineral oil dispersion). Two mililiters of dry light petroleum (bp 30—35°C) was then introduced into the tube through a hypodermic needle, and the suspension was centrifuged. The supernatant was drawn off and the washing was repeated with other two 2-m*l* portions of dry light petroleum. The tube was evacuated to remove the remaining light petroleum and was then flushed with dry nitrogen through hypodermic needles. Two and a half mililiters of dry dimethylsulfoxide was added through a needle, and the mixture was warmed at 70—75°C for 45 min. After the mixture had been cooled to room temperature, to this a solution of 1.79 g of methyltriphenylphosphonium bromide-methyl-^{14}C (5.0 mmol) in dry dimethylsulfoxide was added through a needle. After 10 min, 0.47 g of 2-methylbutanal[*5] (5.5 mmol) was introduced to the solution through a needle, the mixture was then allowed to react for 2 hr at room temperature. The reaction mixture was transferred into a distillation apparatus, and the reaction vessel was washed with non-radioactive 3-methylpentane (0.5 m*l*); the washings were also transferred into the distillation apparatus. Destillation was carried out to collect all of the low-boiling materials in a Dry Ice-acetone-cooled trap. The distillate was treated with a mercuric chloride-mercuric oxide mixture[*6] in ethanol for 2 hr; subsequent distillation afforded a mixture of 3-methylpent-1-ene-^{14}C, 3-methylpentane, and ethanol.

This mixture was hydrogenated using a pre-hydrogenated Adams' platinum oxide catalyst under ordinary pressure at room temperature for 24 hr. The catalyst was then filtered off and washed with non-radioactive 3-methylpentane (0.5 m*l*). To the combined filtrate and washings, a drop of cold conc. sulfuric acid was added and the mixture was stirred at ice-bath temperature. The organic layer was separated, washed with cold aqueous sodium hydrogen carbonate and water, dried over Drierite, and distilled to afford 3-methylpentane boiling at 62—63°C. The overall radioactive

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[*5] Prepared from *s*-butyl magnesium bromide and ethyl orthoformate.

[*6] Mercuric chloride, made alkaline with several drops of sodium hydroxide.

yield was 30.1%.

Preparation of 3-Methyl-pentane-3-methyl-^{14}C. The Wittig reaction of pentanone-3 with methyltriphenylphosphonium bromide-methyl-^{14}C under similar conditions, followed by catalytic hydrogenation, gave the labeled hydrocarbon with a radioactive yield of better than 60%.

Degradation of 3-Methylpentane-1-^{14}C. *i) 3-Bromo-3-methylpentane-1-^{14}C.* The photochemical bromination of a 10.2 g portion of 3-methylpentane-1-^{14}C was carried out using the halogenation apparatus described by Roberts and Mazur[10] with a slight modification. Bromine was introduced into a reaction zone by means of a dry-nitrogen stream bubbling through a bottle containing bromine at room temperature. Irradiation was achieved by a high-pressure mercury lamp (HQ-400Q, Nihon Denchi). After the evolution of hydrogen bromide had ceased, a small portion of solid potassium carbonate was added. The subsequent distillation of the bromination product gave 3-bromo-3-methylpentane-1-^{14}C which boiled at 61.5—62.5°C/59 mmHg (5.63 g). No isomeric monobromides were detected.

ii) 3-Methylpent-2-ene-1-^{14}C. A mixture of 3-bromo-3-methylpentane-1-^{14}C (5.63 g) and water (25 m*l*) in a 50-m*l* flask was refluxed for 10 hr. The organic layer was separated from a cooled reaction mixture, and the aqueous layer was extracted with isooctane. The combined organic layer was dried over potassium carbonate, and distilled to give 3-methylpent-2-ene-1-^{14}C (2.34 g); bp 70.5—73.5°C.

iii) 3-Methylpentane-2,3-diol-1-^{14}C. In a three-necked 100-m*l* flask equipped with a Dimroth condenser, a thermometer, and a serum cap, were placed 18 g of 90% formic acid (0.35 mol) and 4.4 g of 30% hydrogen peroxide (0.04 mol); the mixture was stirred magnetically. A 2.1-g portion of 3-methylpent-2-ene-1-^{14}C (0.025 mol) was added, drop by drop, through a hypodermic needle while the temperature was kept below 45°C. After having been stirred for 1 hr at this temperature, the mixture was allowed to stand overnight at room temperature. Formic acid and water were distilled off under reduced pressure from the reaction flask, and to the residual viscous liquid there was added 20-g portion of sodium hydroxide in 40 m*l* of water under cooling. After stirring for 1 hr, the solution was extracted with six 10-m*l* protions of ether, and the ethereal layer was dried over magnesium sulfate. Ether was then distilled off; the subsequent distillation of the residue gave 3-methylpentane-2,3-diol-1-^{14}C (0.59 g) which boiled at 93°C/16 mmHg.

iv) Degradation of 3-Methylpentane-2,3-diol-1-^{14}C. In a 200-m*l* flask, 0.59 g of 3-methylpentane-2,3-diol-1-^{14}C (5.0 mmol) was oxidized overnight with 1.12 g of sodium metaperiodate (5.25 mmol) in 50 ml of water at room temperature. The reaction mixture was then distilled under reduced pressure, and the distillate was collected in a Dry Ice-acetone-cooled trap to give solution A. A 2-m*l* portion of the solution A was added to a solution of 50 mg of dimedone in 13 m*l* of water. A slight warming was applied, and then the solution was allowed to stand overnight at room temperature. Crystalline precitates were collected and recrystallized from aqueous methanol to afford pure acetaldehyde dimedone, mp 142—142.5°C.

To the remaining portion of the solution A, a slight excess of an aqueous potassium permanganate solution was added. After the reaction had been completed, excess permanganate was decomposed with a few drops of a sodium hydrogen sulfite solution and manganese dioxide formed was filtered off to give filtrate B. To a 10-m*l* portion of the cold filtrate B, 2 g of sodium hydroxide and an iodine-iodide solution containing 1.2 g of iodine and 2.4 g of potassium iodide were added successively. Iodoform was collected by filtration.

To the remaining portion of filtrate B, 0.53 g of 2,4-dinitrophenylhydrazine in 20 m*l* sulfuric acid-aqueous ethanol solution was added, and the precipitates were collected by filtration. Recrystallizations from ethanol afforded methyl ethyl ketone 2,4-dinitrophenylhydrazone, mp 115°C.

The above acidic filtrate was then steam distilled, and the initial 200-m*l* portion of the distillate was collected. Barium carbonate was added to this distillate, and the mixture heated for 24 hr. After cooling, excess barium carbonate was filtered off and the filtrate was evaporated to dryness. After recrystallizations from aqueous ethanol, barium acetate was dried at 120°C under reduced pressure over phosphorus pentoxide.

v) Degradation of Radioactive Barium Acetate. Barium acetate was degraded to carbon dioxide using the apparatus described by Phares.[11] Some modifications were made, however. In the present experiment, two 1 N sodium hydroxide traps were used in order to absorb carbon dioxide. A stream of carbon dioxide-free nitrogen was used to convey the gas evolved. Furthermore, barium carbonate obtained was treated with perchloric acid in an evacuated Barker-type apparatus to regenerate carbon dioxide which was then again fixed with ethanolamine, and the solution was subjected to radioassay.

Destructive Alkylation. A typical experimental procedure of the destructive alkylation will be described. A mixture containing 6.15 g of 3-methylpentane (0.071 mol), 11.2 g of benzene (0.143 mol), 0.95 g of freshly-prepared anhydrous aluminum chloride (0.007 mol), and 0.064 g of water (0.0035 mol) was heated at 100°C in a glass autoclave and agitated. After an appropriate reaction period, the reaction mixture was poured into ice-water and 1 m*l* of conc. hydrochloric acid was added. The organic layer was separated, washed with cold saturated aqueous sodium hydrogen carbonate and then with cold water, and dried over anhydrous magnesium sulfate. In some experiments, *t*-butylbenzene was added in the initial reaction mixture. In this case, *t*-butylbenzene was added to the initial reaction mixture in an amount equal to that expected to be present in a destructive ethylation mixture without any added *t*-butylbenzene (here, 0.265 g).

Analysis of the reaction products by glc indicated the presence of isobutane (a large amount), 2- and 3-methylpentanes, benzene, toluene (small amounts), ethylbenzene (the main product), xylenes (small amounts), and a trace of higher alkylbenzenes. Toluene and xylenes were found to appear when reactions were carried out for 12 hr or longer, although ethylbenzene began to be produced within one hour. In the presence

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[10] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[11] E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

of added *t*-butylbenzene, an increased amount of isobutane was detected by glc; however, no *t*-butylbenzene was present in the product.

Degradation of Radioactive Ethylbenzene. Ethylbenzene was collected by a preparative glc. Oxidation of 0.424 g of radioactive ethylbenzene (4 mmol) with 4.11 g of potassium permanganate (26 mmol) in water (20 m*l*) was performed by heating the mixture for 3 hr. Manganese dioxide was filtered out, and the filtrate and aqueous washings (3 m*l*) were combined. The solution was acidified with conc. hydrochloric acid and extracted with three 10-m*l* portions of ether. Evaporation of ether gave a residue which was recrystallized from water to afford 0.372 g of pure benzoic acid.

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