menthol and neomenthol to form menthenes over alumina catalyst.[9] It is very probable that the formation of nortricyclene over alumina occurs within the pores of alumina so that the hydroxyl group is lost to a surface below the plane of the molecule and the hydrogen to the surface above.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

# Alumina: Catalyst and Support. XVIII.[1] Aromatization of 2,2-Dimethyl-3-methyl-$C^{14}$-pentane over "Non-acidic" Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

BY SIGMUND M. CSICSERY[3] AND HERMAN PINES

RECEIVED MARCH 24, 1962

2,2-Dimethyl-3-methyl-$C^{14}$-pentane was allowed to react at 532–542° over "non-acidic" chromia–alumina catalyst in which the alumina was obtained from potassium aluminate. The aromatic fractions, amounting to about 7 mole % of the reacted trimethylpentane, contained mostly *m*-xylene and toluene. From 71 to 84% of the radioactivity in *m*-xylene was located in the methyl groups, while in toluene 77 to 82% of the radioactivity was in the ring. The radioactivity distribution in *m*-xylene suggests that adsorbed cyclopropane-type intermediates play a major role in the aromatization reaction. Recombination of the products of cracking also contributed to the formation of *m*-xylene. Toluene seems to be formed mostly from 1,1-dimethylcyclohexane-type intermediates through a demethanation reaction.

## 1. Introduction

Extensive study of the aromatization of alkanes over chromia–alumina catalysts has been carried out in our laboratory during the last few years. Since alumina *per se* has intrinsic acidic properties,[4] we were concerned with the influence of the alumina upon the catalytic activity of chromia–alumina catalyst. It was found that a chromia–alumina catalyst which contains alumina prepared from aluminum isopropoxide has relatively strong acidic sites and that this catalyst may cause extensive cationic skeletal isomerization of the dehydrogenated product.[5–7] Dehydrogenation and aromatization proceed, however, without appreciable isomerization over chromia–alumina catalyst where the alumina was obtained from potassium aluminate; to this type of catalyst the name "non-acidic" chromia–alumina was assigned.

The study of the aromatization of *n*-heptane-1-C-14[8,9] and *n*-octane-1-C-14[10] over a "non-acidic" chromia–alumina has suggested that in the transition state adsorbed five-, six-, seven- and, in the case of *n*-octane, also eight-membered ring intermediates were involved.

In order to gain additional insight of the mechanism of aromatization, a systematic study of the behavior of branched $C_6$–$C_8$-hydrocarbons over non-acidic chromia–alumina catalyst was undertaken[6,7] It was found that 2,2-dimethylpentene dehydroisomerized mainly to 2-methylpentenes and 2-methylpentadienes; a small amount of 1,1,2-trimethylcyclopropane was also found in the reaction product. The aromatized product from 2,2,4-trimethylpentane over the "non-acidic" catalyst consisted only of *p*-xylene, while 2,3,4-trimethylpentane yielded all the three xylenes and ethylbenzene. 2,2,3-Trimethylpentane on aromatization produced mainly *m*-xylene and toluene, amounting to about 6 mole per cent. based on the reacted alkane. The aromatization of 2,2,4- and 2,2,3-trimethylpentane was accompanied by an extensive cleavage reaction resulting in the formation of butenes. In the case of 2,2,3-trimethylpentane almost equal amounts of *n*-butenes and isobutylene were produced.[7]

In order to explain skeletal isomerization accompanying the formation of *m*-xylene and toluene from 2,2,3-trimethylpentane, without the participation of a cationic intermediate, it was proposed that the aromatization reaction of branched hydrocarbons may involve adsorbed cyclopropane and cyclobutane-type intermediates.[7] This interpretation was based on the study of many model compounds.

In order to distinguish between these various mechanisms, 2,2-dimethyl-3-methyl-$C^{14}$-pentane was synthesized and aromatized under conditions described previously.[7] The mechanism involving an adsorbed cyclopropane-type intermediate would predict 100% methyl-labeled *m*-xylene and 100% ring-labeled toluene from 2,2-dimethyl-3-methyl-$C^{14}$-pentane (Fig. 1). All the radioactivity will be in the ring if the reaction should proceed through an adsorbed cyclobutane-type transition state (Fig. 2). Recombination of isobutylene and *n*-butene-1-$C^{14}$ will predict 50% radioactivity in the side chains of *m*-xylene (Fig. 3b).

Toluene could be produced either from 1,1-dimethylcyclohexane or from the corresponding olefins.[5] These hydrocarbons can be formed from 2,2,3-timethylpentane through either adsorbed cyclopropane- (Fig. 1) or cyclobutane-type inter-

---

(1) For paper XVII of this series see S. M. Csicsery and H. Pines, *J. Catalysis*, in press (1962).

(2) Paper X of the series "Aromatization of Hydrocarbons," for paper IX see ref. 1.

(3) This research was supported in part by the Atomic Energy Commission, Contract AT(11-1)-1046, and by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of the fund. Taken in part from the Doctoral Thesis of S.M.C., Northwestern University, December, 1961.

(4) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

(5) H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

(6) H. Pines and S. M. Csicsery, *ibid.*, **84**, 292 (1962).

(7) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, in press (1962).

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

(9) C. T. Chen, W. O. Haag and H. Pines, *Chemistry & Industry*, 1379 (1959).

(10) H. Pines and C. T. Chen, "Proceedings of the 2nd International Congress in Catalysis," Paris, 1960, Vol. I, pp. 367–384, published by Editions Technip. Paris, 1961.

mediates (Fig. 2) or by recombination of isobutylene and *n*-butene (Fig. 3c). Each of these mechanisms will predict internally labeled toluene without change of the specific radioactivity. Toluene could also be produced by demethanation of dimethylcyclohexane-type intermediates which may compete at high temperature with dehydrogenation in the aromatization reaction

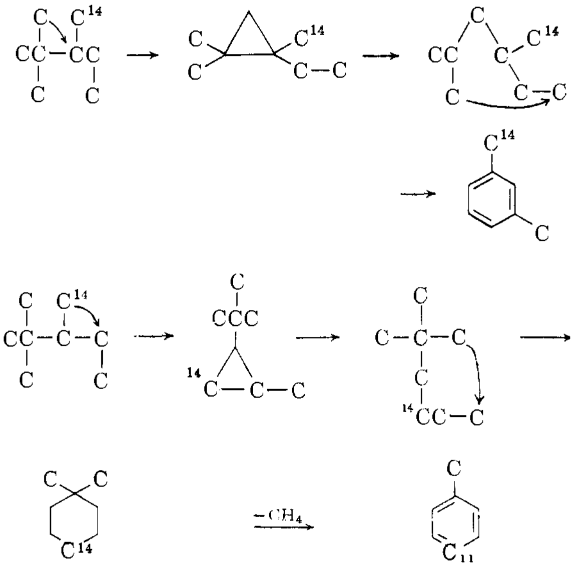


Fig. 1.—Aromatization of 2,2-dimethyl-3-methyl-$C^{14}$-pentane through adsorbed alkylcyclopropane-type intermediates.

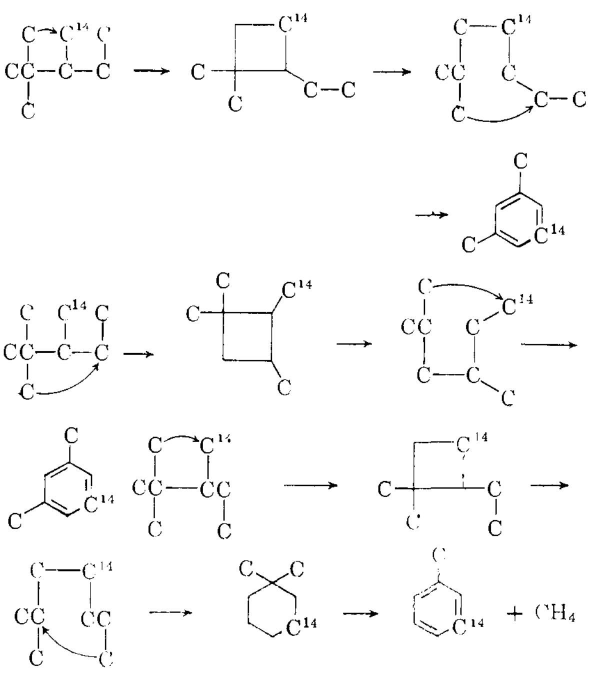
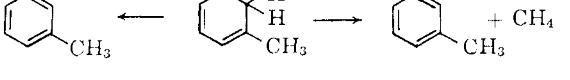


Fig. 2.—Aromatization of 2,2-dimethyl-3-methyl-$C^{14}$-pentane through adsorbed alkylcyclobutane-type intermediates.



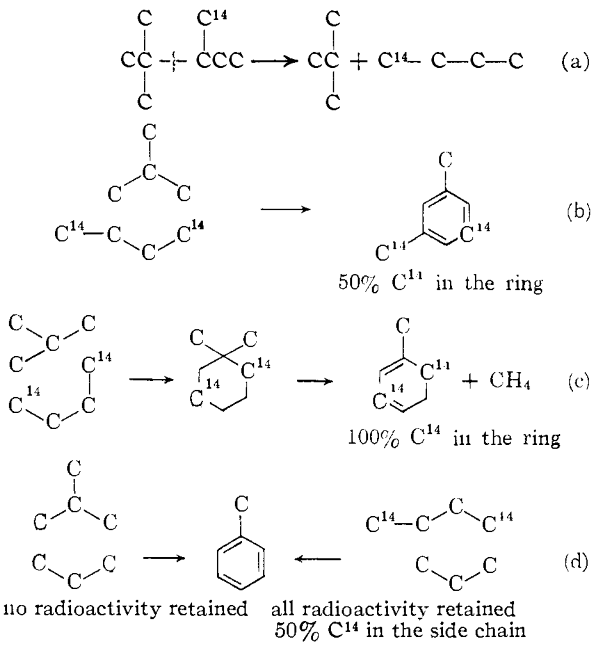


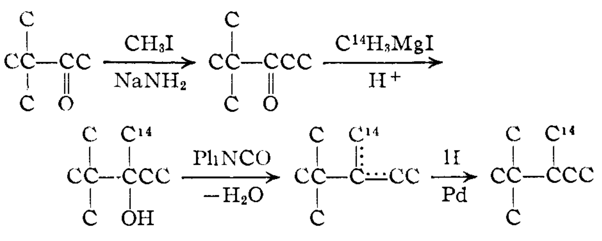
Fig. 3.—Formation of aromatic hydrocarbons through cracking and subsequent recombination of 2,2-dimethyl-3-methyl-$C^{14}$-pentane.

Toluene could also be formed from xylenes under the condition of the dehydrogenation reaction.[7] The toluene formed by demethanation of *m*-xylene or its 1,3-dimethylcyclohexane-type precursor will have lower specific radioactivity than the feed 2,2-dimethyl-3-methyl-$C^{14}$-pentane. The side chain label will depend on the distribution of $C^{14}$ in the *m*-xylene. Recombination of propylene and butenes, a reaction which is less likely to occur, will produce toluene with 0–50% of the $C^{14}$ in the side chain. The specific radioactivity of toluene therefore can be lower than the feed hydrocarbon (Fig. 3d).

The possible aromatization mechanisms for the formation of *m*-xylene and toluene from 2,2-dimethyl-3-methyl-$C^{14}$-pentane are summarized in Table I.

## 2. Procedure

The 2,2-dimethyl-3-methyl-$C^{14}$-pentane was synthesized in 99.3% purity and 18.5% over-all yield by the sequence of reactions



2,2-Dimethyl-3-methyl-$C^{14}$-pentane was dehydrogenated over chromia–alumina catalyst at two different temperatures. Reaction conditions and compositions of the liquid products are summarized in Table II. Experiment 1 product was divided into three nearly equal cuts. Experiment 2 product consisted of a single cut, less than three minutes long. *m*-Xylene and toluene, the principal aromatic products of the reaction, were separated

TABLE I

POSSIBLE DEHYDROCYCLIZATION MECHANISMS FOR THE FORMATION OF *m*-XYLENE AND TOLUENE FROM 2,2,3-TRIMETHYLPENTANE

| Figure | Mechanism | Predicted product | Predicted side chain label from 2,2-dimethyl-3-methyl-$C^{14}$-pentane, % *m*-Xylene | Toluene |
|---|---|---|---|---|
| 1 | Adsorbed cyclopropane-type intermediate | *m*-Xylene<br>Toluene[a] | 100 | $0^b$ |
| 2 | Adsorbed cyclobutane-type intermediate | *m*-Xylene<br>Toluene[a] | 0 | $0^b$ |
| 3b<br>3c | Recombination of $C_4$ cracking products | *o*-, *m*- and *p*-xylene<br>Ethylbenzene and toluene[a] | 50 | $0^b$ |
| 3d | $C_3 + C_4$ recombination | Toluene | | $0–50^c$ |
| | Demethanation of *m*-xylene or 1,3-dimethylcyclohexane-type intermediate | Toluene | | Half of side chain label of *m*-xylene[c] |

[a] Through 1,1-dimethylcyclohexane-type intermediate. [b] All radioactivity retained. [c] Various parts of the radioactivity lost.

using a preparative V.P.C. (vapor phase chromatographic) column. The *m*-xylene and toluene produced were diluted with inactive *m*-xylene and toluene before and after the separations. Total dilution varied from 87- to 1227-fold.

Toluene was oxidized to benzoic acid and *m*-xylene to isophthalic acid by alkaline potassium permanganate. The aromatic acids were decarboxylated in boiling quinoline and the products of the decarboxylation, *i.e.*, benzene and carbon dioxide, were analyzed for radioactivity. Radioactivities of the isophthalic acids and their decarboxylation products are summarized in Table III. The corresponding data for the benzoic acids are given in Table IV. The differences between the radioactivities of the carboxylic acids and the sums of radioactivities of benzenes and carbon dioxides were less than ±4%.

TABLE II

AROMATIZATION OF 2,2-DIMETHYL-3-METHYL-$C^{14}$-PENTANE OVER CHROMIA–ALUMINA CATALYST

| Experiment | ←1→ | | | 2 |
|---|---|---|---|---|
| Cut | 1 | 2 | 3 | |
| Reaction temp., °C. | ←542→ | | | 532 |
| Length of cuts, min., sec. | 10′ | 8′ | 7′40″ | 2′48″ |
| Total feed passed, g. (mmoles) | ←5.75(50.4)→ | | | 0.67(5.9) |
| Liquid product recovered, g. | 1.51 | 1.41 | 1.47 | 0.45 |
| Gaseous hydrocarbons formed, mmoles | ←14→ | | | |
| Hydrogen formed, mmoles | 8 | 6 | 5 | |
| Feed converted to carbonaceous material, wt. % | ←1.15→ | | | |
| Compn. of liquid product, mole % | | | | |
| 2,2,3-Trimethylpentane | 60.0 | 63.5 | 65.0 | 64.0 |
| 2,2,3-Trimethylpentenes | 1.4 | 1.4 | 1.4 | 2.0 |
| Products of cracking (mostly $C_4$) | 37.0 | 33.7 | 32.2 | 32.8 |
| Benzene | 0.10 | 0.09 | 0.09 | 0.08 |
| Toluene | .78 | .67 | .66 | .45 |
| *o*-Xylene | .06 | .06 | .04 | .06 |
| *m*-Xylene | .49 | .39 | .37 | .48 |
| *p*-Xylene | .12 | .12 | .10 | .10 |
| Higher aromatics | .03 | .04 | .04 | .03 |

The experiments were made at an hourly liquid space velocity of 1.38 and at a contact time of 3.1 seconds. The feed hydrocarbon was of 99.3% purity and its radioactivity 7.5 microcurie per millimole.

## 3. Results and Discussion

The percentage of radioactivity located in the methyl groups of *m*-xylene and toluene produced from the aromatization of 2,2-dimethyl-3-methyl-$C^{14}$-pentane is summarized in Table V.

TABLE III

RADIOCHEMICAL ASSAY DATA

DECARBOXYLATION OF ISOPHTHALIC ACID DERIVED FROM *m*-XYLENE PRODUCED BY THE AROMATIZATION OF 2,2-DIMETHYL-3-METHYL-$C^{14}$-PENTANE

| Experiment | ←1→ | | | 2 |
|---|---|---|---|---|
| Cut number | 1 | 2 | 3 | 1 |
| Isophthalic acid decarboxylated, mmoles | 1.44 | 0.82 | 4.03 | 2.90 |
| $BaCO_3$ obtained, mmoles | 2.54 | 1.38 | 7.89 | 5.66 |
| Benzene obtained, mmoles | | | 3.2 | 0.7 |
| $BaCO_3$ yield, mole % | 88.0 | 96.4 | 97.5 | 97.5 |
| Benzene yield, mole % | | | 79 | 24 |
| Radioactivities, $10^{-3}$ $\mu$c./mmole | | | | |
| Isophthalic acid | 28.4 | 44.5 | 10.9 | 6.9 |
| $BaCO_3$ | 10.0 | 16.1 | 4.37 | 2.91 |
| Benzene | | | 2.64 | 1.2 |
| Radioactivity, % | | | | |
| In side chains | 70.5 | 72.5 | 80 | 84.3 |
| In the ring | | | 24 | 17.4 |
| Difference[a] | | | +4 | +1.7 |

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

TABLE IV

RADIOCHEMICAL ASSAY DATA

DECARBOXYLATION OF BENZOIC ACID DERIVED FROM TOLUENE PRODUCED BY THE AROMATIZATION OF 2,2-DIMETHYL-3-METHYL-$C^{14}$-PENTANE

| Experiment | ← 1 → | | 2 |
|---|---|---|---|
| Cut number | 1 | 3 | 1 |
| Benzoic acid decarboxylated, mmoles | 2.5 | 4.75 | 4.62 |
| $BaCO_3$ obtained, mmoles | 0.43 | 0.6 | 4.53 |
| Benzene obtained, mmoles | | 3.46 | 2.6 |
| $BaCO_3$ yield, mole % | [b] | [b] | 98 |
| Benzene yield, mole % | | 73 | 56 |
| Radioactivities, $10^{-3}$ $\mu$c./mmole | | | |
| Benzoic acid | 8.3 | 20.4 | 6.1 |
| $BaCO_3$ | 14.2 | 3.9 | 1.16 |
| Benzene | | 15.7 | 5 |
| Radioactivity, % | | | |
| In the side chain | 17 | 19 | 19 |
| In the ring | | 77 | 82 |
| Difference[a] | | −3 | +1 |

[a] Difference between experimental value and 100% radioactivity recovery. [b] Owing to mechanical losses the yield could not be determined.

TABLE V

PERCENTAGE OF RADIOACTIVITY IN THE *m*-XYLENE AND TOLUENE FORMED FROM THE AROMATIZATION OF 2,2-$Me_2$-3-Me-$C^{14}$-PENTANE

| Experiment | ←1→ | | | 2 |
|---|---|---|---|---|
| Cuts | 1 | 2 | 3 | 1 |
| Radioactivity in side chain, % | | | | |
| *m*-Xylene | 71 | 73 | 80 | 84 |
| Toluene | 17 | | 19 | 19 |

These results have several indications:

a. There is no significant variation in the side chain label between hydrocarbons formed in the different experiments or in the successive cuts of the same experiment. It is therefore unlikely that a "time-dependent" dehydrocyclization plays an important role in the aromatization as in the case of *n*-heptane-1-$C^{14}$[8,9] and *n*-octane-1-$C^{14}$.[9,10]

b. A major part of the *m*-xylene was produced through an adsorbed cyclopropane-type intermediate (Fig. 1).

c. Less *o*- and *p*-xylenes were formed in those cuts where the radioactivity of the ring in *m*-xylene was lower (Table II). Recombination of the cracking products also explains the lower-than-100% side chain radioactivities of the *m*-xylene, as well as the formation of the *o*- and *p*-xylenes.

d. The lower-than-100% side chain radioactivities of the *m*-xylenes may have been caused by some contribution of a dehydrocyclization mechanism proceeding through an adsorbed cyclobutane-type intermediate (Fig. 2). Considering points a and c, contribution from such a mechanism must be unimportant although it cannot be completely excluded.

e. The specific radioactivities of toluene in the different cuts were essentially the same, or only slightly less than that of the feed 2,2-dimethyl-3-$C^{14}$-pentane (Table VI, last line).

f. Point e and the $C^{14}$ distribution show that the toluene produced was not derived solely by dealkylation of the *m*-xylene. The small amount of radioactivity in the side chain of toluene is consistent with a mechanism in which adsorbed alkylcyclopropane intermediates are involved (Fig. 1).

g. The above mechanism will produce only internally labeled toluene; thus a minor part of the toluene had to be formed either by demethylation of *m*-xylene (or its 1,3-dimethylcyclohexane-type precursor) or by recombination of cracking fragments (Figs. 4 and 3 c,d).

h. The carbonaceous materials produced had almost the same specific radioactivity (per g.-atom carbon) as the feed hydrocarbon. Apparently no part of the 2,2,3-trimethylpentane molecule was selectively involved in the formation of the carbonaceous materials.

## 4. Conclusion

The principal products of the aromatization of 2,2,3-trimethylpentane over non-acidic chromia–alumina catalyst are *m*-xylene and toluene. The reaction follows more than one mechanism. In the different cuts of the experiments 41% to 68% of the *m*-xylene was probably formed through an adsorbed cyclopropane-type intermediate (Fig. 1). Recombination of the products of cracking, of iso- and *n*-butenes, is responsible for the formations of most of the rest of the *m*-xylene (Fig. 3b). Adsorbed cyclobutane-type intermediates may have a limited contribution to the aromatization reaction (Fig. 2). A 1,1-dimethylcyclohexane type intermediate seems to be involved in the formation of at least 75% of the toluene produced. The 1,1-dimethylcyclohexane could have been formed either through an adsorbed cyclopropane-type intermediate (Fig. 1), or by the recombination of butenes (Fig. 3c), as suggested by the analogy of the *m*-xylene formation. A minor part of the toluene was produced by the demethanation of *m*-xylene or its 1,3-dimethylcyclohexane-type precursor. Some toluene may have been formed by the recombination of butenes with propylene (Fig. 3d). Due to the moderate concentration of propylene in the reaction product the contribution of this last mechanism should be small.

## 5. Experimental Part

a. **Synthesis of 2,2-Dimethyl-3-methyl-$C^{14}$-pentane.—2,2-Dimethyl-3-pentanone** was prepared according to the general procedure reported previously.[11,12] Pinacolone (111 g., 1.1 moles) was added slowly to a suspension of 44 g. of 90% sodium amide (1 mole) in 300 ml. of ether. After the addition was completed the mixture was refluxed for 3 hours. Methyl iodide (142 g., 1 mole) was then added and the mixture stirred and refluxed for 1 hour. The reaction mixture was allowed to cool and then cautiously poured onto ice. The organic and aqueous layers were separated and the aqueous layer was washed twice with ether. All ether layers were combined, washed with water, dilute sulfuric acid, and again six times with water until neutral, and dried over sodium sulfate. The fraction distilling between 120.5°–127° contained 21 mole % unreacted pinacolone, 61% 2,2-dimethyl-3-pentanone and 18% 2,2,4-trimethyl-3-pentanone. The pure 2,2-dimethyl-3-pentanone was obtained by distillation on a 60-cm. spinning band column; it distilled at 124.5° and was 99.9% pure according to V.P.C. analysis.

**2,2-Dimethyl-3-methyl-$C^{14}$-pentenes.**—A mixture of 0.56 g. of methyl-$C^{14}$ iodide (specific activity: 1.0 mc./mmole; total activity: 4 mc.) and 10 g. of inactive methyl iodide (total: 0.074 mole) in 25 ml. of ether was added slowly to a stirred mixture of 1.93 g. of magnesium (0.08 g.-atom) in 30 ml. of dry ether. After 1.5 hour stirring 8.6 g. (0.075 mole) of 2,2-dimethyl-3-pentanone was added during a period of 2 hours. The mixture was refluxed for 2 hours and allowed to stand overnight. The reaction was carried out under a slow stream of dry nitrogen. The ether solution was poured slowly into a cold solution of 4.4 g. of ammonium chloride in 10 ml. of water. The ether layer was washed once with a dilute sodium bisulfite solution, twice with water and finally with concentrated potassium carbonate solution. After the precipitate in the aqueous layer was dissolved with just enough dilute sulfuric acid to keep the *p*H above 7, it was washed thrice with ether. The combined ether layers were dried over potassium carbonate, and the ether was removed by distillation. The 2,2-dimethyl-3-methyl-$C^{14}$-3-pentanol, which was left in the flask, was dehydrated with 17 g. (0.14 mole) of phenyl isocyanate and 2.2 g. of pyridine, according to procedure described in a previous paper.[7] The olefins thus produced weighed 10.3 g.

**2,2-Dimethyl-3-methyl-$C^{14}$-pentane.**—Olefin (7.451 g.) was hydrogenated in a micro-hydrogenation apparatus over 0.169 g. of Baker 5% palladium-on-charcoal catalyst, diluted with 1.828 g. of inactive 2,2,3-trimethylpentane, and distilled from sodium, using a 60-cm. spinning band micro-column, at 109.8° with 120:1 reflux ratio. The 2,2-dimethyl-3-methyl-$C^{14}$-pentane, 8.14 g., was 99.3% pure, according to V.P.C. analysis. Its radioactivity was 7.5 $\mu$c./mmole (18.5% yield based on methyl-$C^{14}$ iodide used).

b. **Catalyst.**—The chromia–alumina catalyst was prepared according to the procedure described previously.[5] The alumina was precipitated from potassium aluminate

---

(11) A. Haller and E. Bauer, *Ann. chim. phys.*, [8] **29**, 315 (1913).

(12) I. N. Nasarow, *Ber.*, **70**, 594 (1937).

TABLE VI

DILUTION OF *m*-XYLENE AND TOLUENE OBTAINED FROM THE AROMATIZATION OF 2,2-DIMETHYL-3-METHYL-$C^{14}$-PENTANE (ORIGINAL RADIOACTIVITY = 7.5 μc./MMOLE)

| Experiment | ←1→ | | | 2 |
|---|---|---|---|---|
| Cut number | 1 | 2 | 3 | 1 |
| Liquid product recovd., g. | 1.507 | 1.414 | 1.473 | 0.445 |
| *m*-Xylene, wt. % | 0.55 | 0.43 | 0.40 | .53 |
| Toluene, wt. % | .76 | | .63 | .43 |
| *m*-Xylene, g. | .0083 | 0.0061 | .0059 | .0023 |
| Toluene, g. | .0114 | | .0093 | .0019 |
| Inactive diluent added before sepn. on V.P.C. col. | | | | |
| *m*-Xylene, g. | 0.457 | 0.451 | 0.450 | 0.2144 |
| Toluene, g. | 0.239 | | 0.243 | 0.0984 |
| First dilution | | | | |
| *m*-Xylene | 56.2 | 75 | 77.3 | 94.5 |
| Toluene | 22 | | 27.2 | 54.3 |
| Recovd. after separation on V.P.C. column | | | | |
| *m*-Xylene, g. | 0.3163 | 0.3651 | 0.2406 | 0.1590 |
| Toluene, g. | 0.1256 | | 0.1428 | 0.0662 |
| Inactive diluent added before oxidation | | | | |
| *m*-Xylene, g. | 1.2528 | 0.4079 | 2.0409 | 1.6140 |
| Toluene, g. | 0.3702 | | 1.7893 | 1.4301 |
| Second dilution | | | | |
| *m*-Xylene | 4.96 | 2.12 | 9.5 | 11.15 |
| Toluene | 3.95 | | 13.5 | 22.6 |
| Total dilution | | | | |
| *m*-Xylene | 279 | 159 | 735 | 1053 |
| Toluene | 87 | | 367 | 1227 |
| Calcd. activity of diluted *m*-xylene, $10^{-3}$ μc./mmole | 27 | 47 | 10.2 | 7.1 |
| Calcd. activity of diluted toluene, $10^{-3}$ μc./mmole | 86 | | 20.2 | 6.1 |
| Obsd. activity of isophthalic acid, $10^{-3}$ μc./mmole | 28.4 | 44.7 | 10.8 | 6.9 |
| Obsd. activity of benzoic acid, $10^{-3}$ μc./mmole | 83.2 | | 20.1 | 6.1 |

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.

c. **Apparatus and Procedure.**—The apparatus and procedure were the same as described in a preceding paper.[7]

**Separation of Aromatic Hydrocarbons from the Aromatization of 2,2-Dimethyl-3-methyl-$C^{14}$-pentane.**—The separation was done using an F&M model 300 programmed temperature gas chromatograph[13] with a 2.4-m., 1.3-cm. diameter preparative V.P.C. column filled with 7,8-benzoquinoline (5%) on 30/60 mesh Chromosorb; total packing was 614 ml. At 70° temperature, 4 p.s.i. helium inlet pressure and 250 ml./min. helium flow rate, the column had 1040 theoretical plates. The relative retention times at these conditions are: *n*-hexane 1.00; benzene 4.22; toluene 10.70; *m*-xylene 26.50; *o*-xylene 33.50.

Best recovery (up to 98% of injected sample) was achieved by using simple U-tubes of about 1.3 cm. outside diameter immersed in liquid nitrogen; these were connected by Tygon tubing to a second U-tube, also immersed in liquid nitrogen to trap any hydrocarbon which may have gone through the first tube. A calcium chloride tube was attached to the outlet of the second U-tube. The whole system was filled each time with helium before immersing it in the liquid nitrogen trap to prevent condensation of oxygen. The cuts of the dehydrogenation experiments weighed about 1.5 g. and contained approximately 0.5% *m*-xylene and toluene; 0.45 g. of *m*-xylene and 0.24 g. of toluene were added to each sample to ensure sufficient recovery after the separation (Table VI). Each cut was injected in two parts of about 1–1.5 ml. Five fractions were taken: 1, cracking products, 2,2,3-trimethylpentane and 2,2,3-trimethylpentenes; 2, toluene; 3, ethylbenzene, *p*-xylene, if any; 4, *m*-xylene; 5, *o*-xylene.

Fractions 3 and 5 were collected in the same trap, and were so minute that they could not be removed from it without complete loss. Collection of a fraction started when the appearance of the corresponding hydrocarbon was noticed on the V.P.C. recorder chart. The toluene and *m*-xylene fractions were started somewhat later and disconnected somewhat earlier than the respective peaks on the recorder chart started and ended to eliminate contamination of these fractions by any impurities having overlapping peaks. The toluene and *m*-xylene fractions were once again diluted with inactive hydrocarbons before the oxidation. Dilutions of the different fractions varied from 87- to 1227-fold (Table VI).

**Oxidation of Toluene and *m*-Xylene.**—Toluene and *m*-xylene were oxidized with hot alkaline potassium permanganate to benzoic and isophthalic acids as described by Chen.[14] Melting points of the benzoic acids were between 122.8° and 123°. Yields of recrystallized benzoic acids were between 48 and 53%. The isophthalic acid after recrystallization from hot water had melting points between 341.2° and 341.8°. Yields were between 64 and 74%.

*Anal.* of three different samples: Found: C, 57.66, 58.83 and 57.81; H, 3.55, 3.63 and 3.63. Calcd. for $C_8H_6O_4$: C, 57.83; H, 3.64.

Removal of any possible radioactive terephthalic acid was done as described by Chen[14] through the insoluble thallous terephthalate salts.

**Decarboxylation.**—Benzoic and isophthalic acids were decarboxylated by heating in quinoline with copper oxide at 265° for 3 hours according to the procedure outlined by Calvin and his co-workers.[15] Both carbon dioxide and benzene were assayed for $C^{14}$ to obtain the isotope distribution (Tables III and IV). Barium carbonate yields were up to 98.4%, benzene yields varied between 23 and 53%.

All the samples assayed were converted to gaseous carbon dioxide. The organic samples were burned by wet combustion according to the procedure of Van Slyke.[16–18] For compounds such as 2,2-dimethyl-3-methyl-$C^{14}$-pentane dry

---

[13] F & M Scientific Corporation, New Castle, Del.

[14] C. T. Chen, Doctoral Dissertation, Northwestern University, Evanston, Ill., August, 1959.

[15] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 229–230.

[16] D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940).

[17] D. D. Van Slyke, J. Plazin and J. R. Weisiger, *ibid.*, **191**, 299 (1951).

[18] D. D. Van Slyke, R. Steel and J. Plazin, *ibid.*, **192**, 769 (1951).

combustion was preferred.[19] Carbon dioxide from barium carbonate was liberated by hot sulfuric acid.

The radioactivity assay was performed in a 250-ml. DC type 302 stainless steel ionization chamber connected to a vibrating reed Dynacon Electrometer model 600, made by Nuclear–Chicago Corporation. It was equipped with a 10 millivolt G-11 strip-chart recorder, made by Varian Associates, Palo Alto, Calif. Each sample was assayed both by the steady state and by the rate of charge methods. At least two assays were made from each sample. Accuracies of the measurements were within ±0.5–1% for barium carbonate samples, ±1–2% for benzoic and isophthalic acids and ±2.5–5% for benzene samples. This variation is within the accuracy limit of the instrument as indicated by the manufacturer except for benzene. The very small radioactivities of the benzene samples were sometimes only ten times as much as the background current.

**Radioactivity of Carbonaceous Material.**—The carbonaceous material was burned off from the catalyst with an air–nitrogen mixture as described previously.[7] Carbon dioxide was absorbed in 500 ml. of carbon dioxide-free dilute sodium hydroxide solution; 260 ml. of this solution yielded 0.4785 g. of barium carbonate precipitate, which corresponds to 4.66 mmoles of carbon dioxide for the entire carbonaceous material. 2,2,3-Trimethylpentane (50.4 mmoles, with a specific radioactivity of 7.5 μc./millimole) was passed through the catalyst; 4.66 millimoles of $CO_2$ correspond to 4.66/8 = 0.582 mmoles of $C_8H_{18}$, or 1.15% of the total hydrocarbon feed. The radioactivity of the barium carbonate was 0.9 μc./mmole, which is only slightly less than that of the feed, which was 7.5 μc./mmole $C_8H_{18}$, or 0.94 μc./milli-atom C.

---

[19] H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

---

[Contribution from The School of Chemistry, Rutgers, The State University, New Brunswick, N. J.]

# A New Synthesis of Cyclopropanecarboxylic Acids[1,2]

By Donald B. Denney, John J. Vill[3] and Marvin J. Boskin

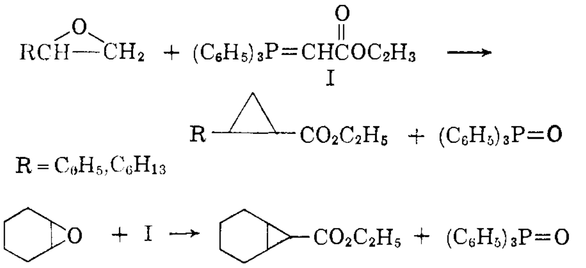
Received May 3, 1962

Carbethoxymethylenetriphenylphosphorane (I) reacts with cyclohexene oxide, 1-octene oxide and styrene oxide to give ethyl norcaranecarboxylate, ethyl *trans*-2-hexylcyclopropanecarboxylate and ethyl *trans*-2-phenylcyclopropanecarboxylate. The yields in these reactions are in the range 30–60%. Optically active styrene oxide and I gave optically active ethyl *trans*-2-phenylcyclopropanecarboxylate. Some mechanistic features of these reactions are discussed.

In recent years the use of phosphoranes as synthetic tools has become increasingly important.[4] This report describes the preparation of substituted cyclopropanecarboxylic esters from carbethoxymethylenetriphenylphosphorane (I) and epoxides.

## Results

Heating a mixture of I and 1-octene oxide at 200° for eight hours gave a 46% yield of ethyl *trans*-2-hexylcyclopropanecarboxylate. These conditions were determined as being optimal for these particular reactants by conducting a series of experiments at different temperatures. Gas–liquid chromatographic analysis of aliquots withdrawn at suitable time intervals indicated that the above conditions led to the highest yields.

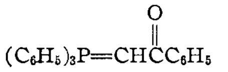


Several potential catalysts for the reaction of I and 1-octene oxide were investigated. It was found that hydroquinone and aluminum isopropoxide had minor catalytic activity. Boron trifluoride etherate inhibited the reaction and triamyl borate had little effect.

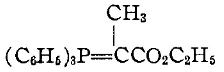
Attempts to conduct the reaction of I and 1-octene oxide in dimethylformamide, diethylene glycol dimethyl ether and nitrobenzene were unsuccessful.

Reaction of I with cyclohexene oxide at 200° (bath) gave a 56% yield of ethyl norcaranecarboxylate. Similarly *dl*-styrene oxide and I gave a 30% yield of ethyl *trans*-2-phenylcyclopropanecarboxylate. In another run, direct conversion to the acid and re-esterification gave a 38% yield. *l*-Styrene oxide and I gave, *via* the acid and then esterification, methyl *l*-*trans*-2-phenylcyclopropanecarboxylate.

Several attempts to use other phosphoranes, II and III, in this reaction were unsuccessful. Triphenylbenzoylmethylenephosphorane (II) did not


$(C_6H_5)_3P{=}CH\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$

II


$(C_6H_5)_3P{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CO_2C_2H_5$

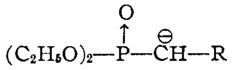
III

react with 1-octene oxide. Some reaction did occur between III and 1-octene oxide as was evidenced by the obtention of >90% yields of triphenylphosphine oxide. The other products appeared to be polymeric and were not characterized.

In another series of experiments, compound I was allowed to react with 1-butene episulfide at reflux, in chloroform at reflux and at room temperature. In each case only unreacted phosphorane and polymeric material was obtained.

## Discussion

Although the reaction conditions required for this synthesis are vigorous, relatively good yields of the desired cyclopropane-containing compounds have been obtained. Recently Wadsworth and Emmons[5] have shown that phosphonate carbanions IV react with epoxides to give substituted cyclopropanes. The carbanions IV are considerably


$(C_2H_5O)_2{-}\overset{\overset{\displaystyle O}{\uparrow}}{P}{-}\overset{\ominus}{C}H{-}R$

IV R = $CO_2C_2H_5$, CN

---

[1] Supported by the National Science Foundation.

[2] A preliminary account appeared in *J. Am. Chem. Soc.*, **81**, 6330 (1959).

[3] National Science Foundation Coöperative Graduate Fellow, 1960–1961.

[4] U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

[5] W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).