[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

An Isotope Effect in the Oxidation of a Secondary Carbinol¹

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When 2-phenyl-1-acenaphthenol-1- C^{14} (I) is oxidized with varying deficient amounts of potassium permanganate, the unoxidized carbinol shows a higher radioactive assay and the oxidation product [8-benzoyl-1-naphthoic-*carboxy*- C^{14} acid (III)] a lower radioactive assay than the starting carbinol (I). This is in accord with a normal isotope effect during the oxidation. That this isotope effect occurred during oxidation of the carbinol to the intermediate 2-phenyl-1-acenaphthenone-1- C^{14} (II), rather than in the further oxidation of this ketone to the acid, is shown by the fact that the ketone itself could be oxidized to the same acid without an isotope effect. Further evidence suggesting the existence of an intermediate ketone during the oxidation of the carbinol is noted in the formation of a derivative of the ketone when the carbinol is oxidized with a deficient quantity of permanganate. A novel use of carbon isotope effect data to elucidate a reaction path is described.

In connection with another problem we have been concerned with the oxidation of 2-phenyl-1acenaphthenol-1- C^{14} (I) and 2-phenyl-1-acenaphthenone-1- C^{14} (II) to 8-benzoyl-1-naphthoic-*carboxy*- C^{14} acid (III). It was discovered that both



I and II could be oxidized to III in good, though not quantitative, yields by the action of neutral, unbuffered permanganate in dilute acetone solution. Furthermore, III could be decarboxylated to non-radioactive 1-benzoylnaphthalene, thus establishing unambiguously the isotopic structures of I, II and III.

The acid III obtained on oxidation of the carbinol I was found to give a radioactive assay reproducibly lower than that of the starting carbinol I. and assaying both unoxidized I and the oxidation product III. The results of these experiments are given in Table I.

Examination of Table I reveals several features: (a) the acid isolated from the oxidation invariably gives a lower radioactive assay than the starting carbinol, (b) the less complete the oxidation, the lower the assay of the oxidation product, and (c) the unoxidized carbinol shows a higher assay than the starting carbinol. These results are in accord with a normal intermolecular isotope effect wherein the 2-phenyl-1-acenaphthenol-1-C¹² is oxidized more rapidly than 2-phenyl-1-acenaphthenol-1-C14. An apparent anomaly appears in Table I. In run No. 2, for example, the recovered carbinol assays 6.2% higher than the starting carbinol, while the acidic oxidation product assays only 4.6% lower than the starting carbinol. Since fully 2/3 of the starting weight of carbinol was recovered in the neutral fraction, one would expect the unoxidized carbinol to show an assay closer to the starting carbinol than does the acidic product. Actually the reverse is true. An explanation of this anomaly is given in a later paragraph.

TABLE I

OXIDATION OF 2-PHENYL-1-ACENAPHTHENOL-1-C¹⁴ WITH VARYING QUANTITIES OF POTASSIUM PERMANGANATE

No.	Wt. I,ª g.	Wt. KM104, g.	Equiv. KMnO₄ Equiv. I		Acid	, III	Neutral fraction	
				Yield, g.	Vield, b %	Assay, µc./mmole	Yield, g.	Assay, ε μc./mmole
1	0.40	0.18	0.35	0.09	20.0	2.179 ± 0.043^{d}	0.31	2.420 ± 0.003^{d}
2	.40	.26	0.50	.15	33.4	$2.218 \pm .012^{d}$.27	$2.468 \pm .009^{d}$
3	.20	.26	1.00	.17	75.5	$2.238 \pm .014^{d}$.04	· · · · · · · · · · · · · · · · · · ·
4	.20	.29	1.10	.18	80.0	2.230°	.04	
5	.20	.52	2.00	.21	93.4	$2.290 \pm .010^{d}$.04	• • • • • • • • • • • • • •

^a Radioactive assay, $2.326 \pm 0.016 \ \mu c./mmole.$ ^b Based on weight of acid theoretically obtainable from I. ^c Assay of pure I isolated from neutral fraction. ^d Average deviation from mean value of two or more determinations. Experimental error estimated as $\pm 0.5 - 1.0\%$. ^e Single determination.

After elimination of explanations for this discrepancy such as purity and identity of III, instrumental error, and statistical variation, it was concluded that the low assays of the III derived from I were due to an isotope effect during the oxidation. Further experiments designed to test the validity of this hypothesis showed it to be indeed correct.

The experiments demonstrating conclusively the presence of such an isotope effect consisted in conducting such oxidations of I in the presence of varying quantities of permanganate, then isolating

(1) This paper is based upon work performed under contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory. Attention was next directed to the possibility of an isotope effect in the oxidation of the ketone II to the acid III. Table II indicates that both the unoxidized fraction and the acidic fraction gave radioactive assays identical within experimental error to that of the starting ketone. In short, no isotope effect was apparent in this oxidation. The unoxidized material in run No. 2 of Table II, however, was not unchanged 2-phenyl-1-acenaphthenone-1- C^{14} , m.p. 115–116.5°, but rather a sparingly soluble substance of m.p. 238–239°. This same high melting material appeared in several other instances in the present investigation. In both the aluminum chloride catalyzed cyclization

OXIDATION OF	Z-PHENYL-	I-ACENAPHI	HENONE-1-	C ¹⁴ WITH VA	RYING QUANTITIES OF	F POTASSIUM	PERMANGANATE
	Wt	Equiv. KMnO4	Acid, III			Unoxidized material	
. Wt. II,ª g.	KMnO4, g.	Equiv. II	Yield, g.	Yield, %	μc./mmole	Yield, g.	$\mu c./mmole$
0.20	0.20	1.12	0.18	80.0	$2.341 \pm 0.003^{\circ}$	0.03	
.40	.19	0.50	.15	33.2	$2.339 \pm .015^{\circ}$.23	$2.317 \pm 0.011^{\circ}$
	. Wt. II, ^a g. 0.20 .40	Wt. II, ^a g. KMnO ₄ , g. 0.20 0.20 .40 .19	Wt. II,4 g. KMnO4 Equiv. Equiv. Wt. KMnO4 Equiv. II 0.20 0.20 1.12 .40 .19 0.50	Wt. II, 4 g. KMnO4 0.20 0.20 1.12 0.18 .40 .19 0.50 .15	WITH VA Equiv. Acid, Wt. KMnO4 Wt. KMnO4 Second Sec	WITH VARYING QUANTITIES OF 2-PHENYL-1-ACENAPHTHENONE-1-C ^{A4} WITH VARYING QUANTITIES OF Equiv. Equiv. Acid, III Wt. KMnO4, g. KMnO4, g. Equiv. II Yield, g. Yield, % Acid, III Wt. II, ⁴ g. KMnO4, g. Equiv. II Yield, g. Yield, % $\mu c./mmole$ 0.20 0.20 1.12 0.18 80.0 2.341 ± 0.003° .40 .19 0.50 .15 33.2 2.339 ± .015°	WITH VARYING QUANTITIES OF POTASSIUM Equiv. Unc Wt. Assay. Wt. Minor Minor Minor Minor Assay. Minor Minor Minor Assay. Minor Assay. Minor Assay. Minor Assay. 0.20 0.18 80.0 2.341 ± 0.003° 0.03 .40 .19 0.50 .15 33.2 2.339 ± .015° .23

TABLE II

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^a Radioactive assay, $2.322 \pm 0.002 \,\mu$ c./mmole. ^b Calculated as the aldol. IV. ^c Average deviation from mean value of two or more determinations. Over-all experimental error estimated as $\pm 0.5-1.0\%$.

of phenyl- α -naphthylacetyl-1-C¹⁴ chloride to produce II and in the lithium aluminum hydride reduction of II to the carbinol I, this same high melting substance was produced in small amounts. Similarly, it was found that the action of ethoxide ion in ethanol on the ketone II gave rise to small amounts of the same product. This product showed the correct radioactive assay, carbon and hydrogen content, active hydrogen content, and molecular weight for IV, the aldol condensation product of the ketone II.

0.5



Since the identity of IV was not of major interest to us, we have assumed its structure on the basis of the data mentioned, and have made no attempt to establish the structure unambiguously by other means.

Referring to the previously mentioned anomalously high assay for the unoxidized carbinol in run No. 2 of Table I, if one calculates the extent of oxidation necessary to give a radioactive balance, assuming the acid III to be the sole product, the calculated figure is 58%. The amount of acid III isolated, however, corresponds only to 33%oxidation. A like calculation for run No. 1 gives a similar result. These calculations suggested that one or more neutral products besides carbinol must have been present in the crude non-acid fraction. Such a situation would arise, for example, if the course of the oxidation were: carbinol (I) \rightarrow ketone (II) \rightarrow acid (III) and if the second oxida-tion stage were incomplete. Accordingly we examined the mother liquors from one of the carbinol oxidations for a second neutral product, and indeed were able to isolate small quantities of the aldol IV, which in turn was oxidizable to the acid III only very slowly. Since IV was produced in the incomplete oxidation of the ketone, the isolation of IV in the present instance provides evidence that the ketone is, as might be expected, an intermediate in the oxidation of the carbinol to the acid. Since the ketone itself has been shown to produce the acid with no isotope effect, it follows that the isotope effect in the over-all oxidation of the carbinol must have occurred in its transformation to the intermediate ketone.

Thus in the present instance isotope effect data have been used to predict the presence of a reaction intermediate and to elucidate a reaction path. To our knowledge this is the first example of such a use of a carbon isotope effect.

Isotope effects involving carbon during oxidation have been reported only in a few instances in the past and never, as in the present instance, in a system where the oxidized group remains attached to the unoxidized moiety. Evans and Huston have reported² an isotope effect in the oxidation of acetic-1-C14 acid to carbon dioxide and water by means of Van Slyke solution, on the basis of their observation that the initial carbon dioxide evolved was isotopically depleted. This interpretation is open to question however, since it is possible that the methyl and carboxyl moieties of the acetic-1-C14 acid are oxidized to carbon dioxide at different rates. Armstrong co-workers report³ an isotope effect in the oxidation of C¹⁴labeled urea and urea nitrate; an isotope effect in the oxidation of oxalic-C14 acid with a variety of oxidants has recently been unambiguously established.⁴ Unfortunately, the occurrence of a side reaction and the general complexity of our present oxidation-reduction system preclude the possibility of any quantitative treatment of the present example. Investigations of such oxidations in simpler systems are now in progress.

Experimental

Phenyl-\alpha-naphthylcarbinol.—Benzoylnaphthalene⁶ (131.3 g.) was dissolved in dry ether (400 ml.) and the solution added dropwise with stirring to a slurry of lithium aluminum hydride (11.3 g.) in ether (400 ml.) contained in a five-liter three-necked flask equipped with reflux condenser and calcium chloride tube. Stirring was continued for 20 minutes after addition, after which the excess hydride was consumed by the dropwise addition of excess ethyl acetate. 10% sulfuric acid (200 ml.) was next added dropwise, then concd. hydrochloric acid (*ca.* 40 ml.). The layers were separated and the aqueous layer extracted once with ether. The washed ether layers were dried (Na₂SO₄) and the solvent distilled to give 138 g. of clear oil. This was crystallized from a mixture of benzene (50 ml.) and ligroin (400 ml.) to give 125.5 g. (95%) of the desired carbinol, m.p. 88-89°, in agreement with the literature.⁶

Phenyl- α -naphthylacetic-carboxy-C¹⁴ Acid.—Phenyl- α -naphthylcarbinol (125.5 g.) was refluxed for 1.5 hours with thionyl chloride (200 ml.), after which the excess of the latter was removed *in vacuo* at 100°. The dark residue was dissolved in benzene (250 ml.), and again distilled *in vacuo* to dryness. Radioactive cuprous cyanide (48.4 g., 1 equiv.) (prepared by adaptation of the procedure of Barber⁷; assay ca. 3.5 μ c/mmole) was added to the above benzene distillation residue, and the resulting slurry was placed in an in-tained at 200–210° and the reaction vessel swirled occa-

(7) H. J. Barber, J. Chem. Soc., 79 (1943).

⁽²⁾ E. A. Evans and J. L. Huston, J. Chem. Phys., 19, 1214 (1951).
(3) W. D. Armstrong, L. Singer, S. H. Zbarsky and B. Dunshee, Science, 112, 531 (1950).

⁽⁴⁾ C. A. Bunton and D. R. Llewellyn, Research, 5, 443 (1952).

⁽⁵⁾ L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Co., Boston, Mass., 1941, p. 192.

⁽⁶⁾ M. W. D. Cohen, Rec. trav. chim., **38**, 120 (1919).

sionally during a two-hour period. The melt was cooled, dissolved in acetone, and the solids filtered (Celite) rinsing well with acetone. Solvent evaporation from the filtrate gave 137 g. (104%) of crude phenyl- α -naphthylacetonitrilel-C¹⁴. This was stirred vigorously for four hours with refluxing 50% sulfuric acid (500 ml.). After cooling, the organic material was dissolved in hot benzene and the aqueous layer extracted four times with hot benzene (total benzene volume 600 ml.). Cooling produced 58 g. of crude acid, m.p. 108-112°. The benzene filtrate was extracted twice with hot 20% sodium hydroxide solution, then discarded. The alkaline extract was acidified, cooled and extracted with ether. The ether solution was washed with water, dried (Celite) and decolorized by filtration through Norit. Solvent removal produced 76 g. amber sirup, giving a total crude yield of 99%. The combined crude material was recrystallized from a 1:1.4 methanol-benzene mixture (240 ml.). Successive crops were taken, such that the yield of recrystallized material totalled 113.2 g. (81%), with a maximum m.p. of 138.5-139.5°. McKenzie and Tattersall⁸ report m.p. 140-141° for pure phenyl- α -naphthylacetic acid.

2-Phenyl-1-acenaphthenone-1-C14.--This was prepared by a modification of the procedure of Koelsch and Richter. Phenyl- α -naphthylacetic-*carboxy*-C¹⁴ acid (96.5 g.) was re-fluxed with thionyl chloride (200 ml.) for two hours. The excess thionyl chloride was distilled, last traces at 2 mm. The dark residue (90.3 g.) was dissolved in dry benzene (200 ml.) and the solution added dropwise with stirring over a 20-min. period to a refluxing slurry of benzene (300 ml.) and aluminum chloride (55 g.). Stirring and reflux were continued for one hour, whereupon the mixture was cooled and treated with ice and dilute hydrochloric acid. The benzene layer was washed, dried and freed of solvent to give 101.5 g. of dark oil. This was distilled at 2 mm. through a short-path still and the middle fraction, 55 g. collected from 150–190°. The distilled sirup was crystallized from a mixture of ether and ligroin to produce 25.2 g. of crude product, m.p. 116-118°. An additional 2.3 g. of less pure material resulted from the mother liquors, totalling 27.5 g. (31%). The product was purified by two recrystallizations from a 1:10 acetone-ligroin mixture, giving pure 2-phenyl-1-acenaphthenone-1-C¹⁴, m.p. 115–116.5°. Koelsch and Richter report⁹ m.p. 115.5–116.5°.

Assay: Found: 2.324, 2.320; average, 2.322 \pm 0.002 $\mu c/mmole.$

The mother liquors from the above purification were decolorized by filtration through Norit. On prolonged standing they produced 1.5 g. of higher melting solid. This was recrystallized from acetone to give 0.22 g. of a pure sample of what was apparently the aldol (IV) of 2-phenyl-1acenaphthenone-1-C¹⁴, m.p. 239–241°.

Anal. Caled. for $C_{36}H_{24}O_2$: C, 88.52; H, 4.95; active H, 0.206; mol. wt., 488. Found: C, 88.58; H, 4.88; active H, 0.19; mol. wt., 495.

2-Phenyl-1-acenaphthenol-1-C¹⁴.—2-Phenyl-1-acenaphthenone-1-C¹⁴ (16.0 g.) was dissolved in ether (500 ml.) and the solution added dropwise with stirring to a slurry of lithium aluminum hydride (1 g.) in ether (50 ml.). Stirring under reflux was continued for 20 minutes after the addition, following which the unreacted hydride was consumed by dropwise addition of excess ethyl acetate. Water was added dropwise and finally dilute sulfuric acid. At this point 8.5 g. of crude product was filtered; m.p. 165.5-166.5°. The filtrate was separated and the ether layer was washed, dried and freed of solvent to produce 8.0 g. of semisolid paste. The latter was crystallized from a mixture of acetone and ligroin to give 1.6 g. of solid; m.p. 160–162°. Evaporation of the mother liquors produced 5.6 g. of sirup. The combined crystalline material was purified by recrystallization from a mixture of acetone (150 ml.) and ligroin (250 ml.) to give 7.8 g. of pure carbinol; fine needles of m.p. 166.5–167.7° on evaporation to 100 ml.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.26, 87.23; H, 5.86, 5.80. Assay: Calcd.: 2.322 μ c mmole. Found: 2.305, 2.318, 2.350; average, 2.326 \pm 0.016 μ c mmole. The 5.6 g. of sirup above was dissolved in acetone and ligroin and allowed to stand. Over a period of time about 1 g. of aldol IV separated. Recrystallization gave material of m.p. 239-241° which showed no mixed m.p. depression and an identical infrared absorption spectrum (between 5-15 μ c in mineral oil mull) with the by-product isolated above in the cyclization producing 2-phenyl-1-acenaphthenone-1-C¹⁴. Assay: Calcd. for C₃₆H₂₄O₂: 2.322 μ c mmole. Found: 2.315 μ c mmole.

The Oxidation of 2-Phenyl-1-acenaphthenol-1-C¹⁴.—The above carbinol (0.20 g.) was dissolved in acetone (10 ml.). To this was added a solution of potassium permanganate (0.26 g., theoretical quantity) in water (5 ml.). The last traces of the oxidant were rinsed in with additional acetone (5 ml.). The oxidation mixture stood at room temperature for 3.5 hours, after which the MnO₂ was filtered and rinsed with acetone. The filtrate was heated just to boiling and allowed to cool twice. The MnO_2 was again filtered, and the slight remaining permanganate color in the filtrate discharged with a drop of bisulfite solution. The mixture was placed in an air stream to evaporate the acetone, and the residue diluted with water A small quantity of ether was added and the mixture stirred thoroughly during the addi-tion of excess solid sodium carbonate. The layers were separated. Evaporation of the ether layer led to 0.04 g. of amber solid. The carbonate layer was acidified and the precipitated acid extracted into the two solution in the precipitated acid extracted into ether. Solvent removal produced 0.17 g. (76%) of crude 8-benzoyl-1-naphthoic-carboxy-C¹⁴ acid. Two recrystallizations from a mixture of ether and ligroin gave the pure product; m.p. 130.5° in agreement with the literature.^{10,11}

Assay: Calcd. for $C_{18}H_{12}O_3$: 2.322 μ c mmole. Found: 2.220, 2.215, 2.255, 2.248, 2.250; average, 2.238 \pm 0.014 μ c mmole.

In general the data recorded in Table I were obtained by conducting the oxidation in the fashion described above, except that varying quantities of oxidant were employed. In cases where the unoxidized carbinol was assayed, the crude neutral fraction from the oxidation was recrystallized from an acetone-ligroin mixture, and the resulting carbinol found to have the correct m.p. In run No. 4 of Table I the mother liquors from the recrystallization of the unoxidized carbinol were evaporated to dryness and the residue boiled with a small amount of acetone. Crystallization resulted in 0.01 g. of the aldol IV. This was purified by grinding under warm acetone; m.p. 233-234°. It gave no mixed m.p. depression and an identical infrared absorption spectrum with the previously isolated samples.

Oxidation of 2-Phenyl-1-acenaphthenone-1-C¹⁴.—The oxidations giving the data in Table II were conducted in the manner described above. In run No. 2 the unoxidized material proved to be the aldol IV, m.p. 238–239° after two recrystallizations from an acetone-ligroin mixture. The sample showed no mixed m.p. depression and an identical infrared pattern with the previously isolated products.

Oxidation of the Aldol IV.—The by-product obtained in the preparation of the 2-phenyl-1-acenaphthenol- $1-C^{14}$ above (0.10 g.) was oxidized in the usual manner with permanganate (0.09 g.). In contrast with oxidations of the carbinol and ketone, the present reaction was extremely slow. After three days considerable permanganate color remained, and the mixture was processed in the previously described fashion. The neutral fraction consisted of 0.07 g. which on recrystallization gave 0.03 g. of unchanged starting material, m.p. 231–233°.

Assay: Calcd.: 2.322 μ c/mmole. Found: 2.360, 2.375; average, 2.368 \pm 0.008 μ c/mmole.

The acid fraction, obtained as usual, weighed 0.02 g. Recrystallization from an ether-ligroin mixture gave reasonably pure 8-benzoyl-1-naphthoic-*carboxy*- C^{14} acid, m.p. 128–130°.

Assay. Calcd. for $C_{18}H_{12}O_3$: 2.322 µc/mmole. Found: 2.270 µc/mmole.

Unfortunately the small quantity of material and questionable purity of the acid do not provide unambiguous evidence for an isotope effect during this oxidation. The assays, however, do suggest that an isotope effect may be present in the oxidation of the aldol IV.

(11) E. Ghigi. Ber., 73B, 700 (1940).

⁽⁸⁾ A. McKenzie and H. S. Tattersall, ibid., 2527 (1925).

⁽⁹⁾ C. F. Koelsch and H. J. Richter, THIS JOURNAL, 59, 2165 (1937).

⁽¹⁰⁾ W. Knapp, Monatsh., 67, 336 (1946).

Decarboxylation of 8-Benzoyl-1-naphthoic-carboxy-C¹⁴ Acid.—The acid (0.15 g.) having an assay of 2.238 μ c/ mmole was dissolved in quinoline (3 ml.) and treated with a pinch of copper chromite. The mixture was refluxed for 25 minutes while sweeping the system with helium which passed on exit through saturated barium hydroxide solution. The barium carbonate precipitated was filtered, rinsed with boiled water, and dried at 135° (1 mm.) for five hours. It weighed 0.07 g. (66%).

Assay. Calcd. 2.238 μ c/mmole. Found: 2.156, 2.100; Average 2.128 \pm 0.028 μ c/mmole.

The low assay here is undoubtedly due to coprecipitation contamination of the barium carbonate.

The quinoline residue was rinsed into water, strongly acidified with hydrochloric acid, and the mixture extracted continuously with ether for 4.5 hours. Solvent evaporation left 0.14 g. of amber oil. This was recrystallized from methanol with decolorization and seeding to produce 0.02 g. of benzoylnaphthalene, m.p. 75.6°, no mixed m.p. depression

with an authentic sample. Assay showed the material to be completely void of radioactivity.

Action of Sodium Ethoxide on 2-Phenyl-1-acenaphthenone-1-C¹⁴.—The ketone (0.15g.) in absolute ethanol (10 ml.)was treated with two drops of *ca.* 1.5% sodium ethylate solution. An immediate purple coloration was noted. On standing overnight, the color was discharged and the product had begun to crystallize from the solution. Another two drops of ethylate solution was added and the mixture again allowed to stand until colorless. This process was repeated until the further addition of ethylate engendered no coloration. The solid was filtered and rinsed with ethanol, 0.04 g., m.p. 237–239°. On concentration of the mother liquor an additional 0.02 g. of impure material resulted. The pure material showed an infrared spectrum identical with the previous high-melting product.

Assay. Calcd. for C_{35}H_{24}O_2: 2.322 $\mu c/mmole.$ Found: 2.300 $\mu c/mmole.$

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Isomerization Accompanying Alkylation. IX.¹ The Reaction of Benzene with n- and Isopropylcyclopropane. The Synthesis of n- and Isopropylcyclopropane²

By Herman Pines, William D. Huntsman^{3a,3b} and V. N. Ipatieff^{3c}

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The alkylation of benzene with *n*- and isopropylcyclopropane in the presence of hydrogen fluoride has been studied. The reaction of benzene with *n*-propylcyclopropane produced a mixture of hexylbenzenes consisting of approximately 41% 2- and 46% 3-phenylbenzene. With isopropylcyclopropane, the monoalkylated product consisted of approximately 80% 2-methyl-2-phenylpentane and possibly as much as 15% 3-methyl-3-phenylpentane. The three-membered ring in monoalkylcyclopropanes appears to cleave exclusively in one direction during acid-catalyzed alkylations. The synthesis of *n*and isopropylcyclopropane in good yields and the infrared spectra of these compounds are reported. The infrared spectra of four of the hexylbenzenes are reported.

The acid-catalyzed alkylation of benzene with cyclopropane at low temperatures is of interest because n-propylbenzene is formed to the exclusion of the isopropyl derivative.4,5 Recent studies in this Laboratory, however, have shown that extensive isomerization of the type involving hydride ion shifts occurs during the alkylation of benzene with certain alkylcyclopropanes.⁵ Ethylcyclopropane, for example, yields a mixture of 2- and 3phenylpentane, this formation of the former involving an hydride ion shift. The production of the same mixture of pentylbenzenes during the alkylation of benzene with 2- or 3-pentanol1 further exemplifies the ease with which this isomerization occurs. The formation of these substances to the exclusion of the other possible isomeric pentylbenzenes, coupled with the fact that the alkylation of benzene with methylcyclopropane furnishes pure s-butylbenzene, indicates that the threemembered ring cleaves exclusively in one direction during acid-catalyzed alkylations. This mode of

(1) For paper VIII of this series, see: H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4483 (1951).

(2) Presented, in part, before the Organic Division of the American Chemical Society, Chicago, Ill., Sept., 1950.

(3) (a) Universal Oil Products Co. Predoctoral Fellow, 1947-1950;
(b) abstracted, in part, from the Ph.D. thesis of W.D.H.; August, 1950;
(c) deceased November 29, 1952.

(4) J. H. Simons, S. Archer and E. Adams, THIS JOURNAL, **60**, 2955 (1938); V. N. Ipatieff, H. Pines and B. B. Corson, *ibid.*, **60**, 577 (1938); V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); A. V. Grosse and V. N. Ipatieff, *ibid.*, **2**, 447 (1937).

(5) H. Pines, W. D. Huntsman and V. N. Ipatieff, This JOURNAL, 73, 4343 (1951).

cleavage is illustrated by the equation

$$R \xrightarrow{H} CH_{2} H^{+} \longrightarrow R \xrightarrow{+} CH \xrightarrow{+} CH_{2} - CH_{3}$$

This study has now been extended to include nand isopropylcyclopropane. With these compounds it was found that the cyclopropane ring cleaves by the scheme outlined above, and extensive isomerization occurred during alkylation. Thus, the reaction of benzene with *n*-propylcyclopropane catalyzed by hydrogen fluoride produced a mixture of hexylbenzenes consisting of approximately 41% 2- and 46% 3-phenylhexane as determined by infrared analysis (Fig. 1). All of the bands present in the spectrum of the alkylated product are present in the spectra of either 2- or 3phenylhexane. Hence, the spectrum of the impurity must be weak or else very similar to the spectra of 2- or 3-phenylhexane. The spectra of the latter compounds are very similar and it was necessary to resort to secondary bands at 9.94, 11.34 and 12.40 μ for analytical calculations.

The alkylation product from isopropylcyclopropane and benzene (Fig. 2) consisted of approximately .80% 2-methyl-2-phenylpentane (I) (Fig. 3) and may contain as much as 15% 3-methyl-3phenylpentane (II)⁶ (Fig. 4). According to infrared spectra 2-methyl-3-phenylpentane was not

(6) Sample furnished by the Universal Oil Products Co.