TABLE IV

PROPERTIES OF VARIOUS SAMPLES OF PHENANTHRENE

Sample	Description of sample	Known impurities (wt. per cent.) Anthracene	Carbazole	Fluorene	Freezing point, °C. Observed	Corrected for known impurities
1	Commercial, as received	9.4	3.8	2.0	100.85	(88.7)
2	Commercial, treated with maleic anhydride and sodium and twice recrystallized	0.065	0.3	Present	98.963	98.01
3	Sample 2 distilled azeotropically and twice recrystallized	.093	.00	0.00	99.177	99.113
4	Commercial, treated with maleic anhydride and distilled azeotropically	.86	.00	.00	99.459	98.909
5	Synthetic	.75	.00	.00	99.621	99.152

phenanthrene containing 0.75% anthracene was 99.621°. When corrected for the anthracene content, the freezing point was 99.152°, compared with 99.113° found for phenanthrene purified by azeotropic distillation. Recrystallization of the synthetic phenanthrene from ethanol increased the anthracene content to 1.06% (ultraviolet spectrometry) and also raised the freezing point to 99.812°. As the increase of 0.31% of anthracene, indicated by ultraviolet spectrometry, should increase the freezing point by 0.31 × 0.625 = 0.194°, and as an actual increase of 0.191° was observed, the cryoscopic and ultraviolet data are self-consistent.

Purification of Phenanthrene by Azeotropic Distillation. A. Chemically Purified Phenanthrene.—The sample of phenanthrene which had been purified by chemical methods was distilled with excess diethylene glycol in a 4-ft. long, 1-in. diameter heli-grid column, first at 100 mm., then at 20 mm. pressure. The distillate fractions were mixed with four to five times their volumes of water to precipitate the hydrocarbons which were filtered by suction and washed well with water. The aqueous filtrate was concentrated by evaporation on a steam-bath and then vacuum distilled to recover the glycol. The small quantity of solid (impure fluorene?) recovered from the first fraction had a melting point of 89–92°. Dilution of the residue with water precipitated the carbazole which, after crystallization from aqueous alcohol, melted at 242–245°. The middle third of the distillate, containing the bulk of the phenanthrene, was precipitated, filtered, washed, and recrystallized twice from alcohol to remove occluded glycol. In the final crystallizations, the phenanthrene was centrifuged and washed with ice-cold alcohol. The freezing point of this material was 99.141 ± 0.003°. Further crystallization from alcohol resulted in increasing the freezing point to 99.179 ± 0.003° as determined by cooling and warming curves. Ultraviolet analysis showed the presence of 0.093% anthracene. The exact purity could not be estimated because of the possibility of the presence of undetected impurities which form solid solutions. It appeared, however, that the sample was very pure since it froze sharply over an extremely narrow temperature range. When impurities are present, the range is much greater, whether solid solutions are formed or not, and it becomes more difficult to determine freezing points by warming curves.

B. Commercial Phenanthrene.—In the preferred procedure, a 580-g. sample of commercial (80%) phenanthrene was refluxed with 165 g. of maleic anhydride in xylene solution, the mixture filtered, the filtrate extracted with alkali, and the xylene evaporated. The residue of 558 g. was distilled with excess diethylene glycol from a 5-liter flask through a 3-ft. long, 1-in. diameter heli-grid column. The fractions were precipitated by dilution with water, the separated solids were centrifuged, washed well with water, and dried at 65°. Some of the fractions were dissolved in a small quantity of acetone and reprecipitated with water, others were crystallized from alcohol. The fractions and their properties are listed in Table III.

The best sample of phenanthrene, obtained from this distillation, had a freezing point of 99.459° and contained 0.86% anthracene. The properties of the various samples of phenanthrene described in these experiments appear in Table IV.

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

Isomerization Accompanying Alkylation. VII.[1] Reaction of Benzene with Methylcyclopropane, Ethylcyclopropane and with Dimethylcyclopropanes

BY HERMAN PINES, WILLIAM D. HUNTSMAN[2a,2b] AND V. N. IPATIEFF

The alkylation of benzene with methyl-, dimethyl- and ethylcyclopropanes was studied. Methylcyclopropane reacted with benzene in the presence of hydrogen fluoride to give pure *s*-butylbenzene. Ethylcyclopropane reacted with benzene in the presence of hydrogen fluoride, sulfuric acid and aluminum chloride. The monoalkylated product consisted in each case of about 63% of 2- and 37% of 3-phenylpentane. 1,1-Dimethylcyclopropane with benzene in the presence of hydrogen fluoride formed *t*-amylbenzene, while 1,2-dimethylcyclopropane gave *t*-amylbenzene and smaller amounts of 2- and 3-phenylpentane, and 2-phenyl-3-methylbutane. The infrared spectra of six of the amylbenzenes are reported.

The alkylation of benzene with compounds containing a cyclopropane ring has received relatively little study. The only examples reported in the literature are those in which cyclopropane itself was used as the alkylating agent. In the presence of hydrogen fluoride,[3] aluminum chloride[4] or sulfuric acid[5] catalysts at low temperatures (0–35°) the sole monoalkylated product isolated was *n*-propylbenzene. With a sulfuric acid catalyst at 65°, the monoalkylated product consisted of isopropylbenzene.[4a]

The complete absence of isopropylbenzene in the

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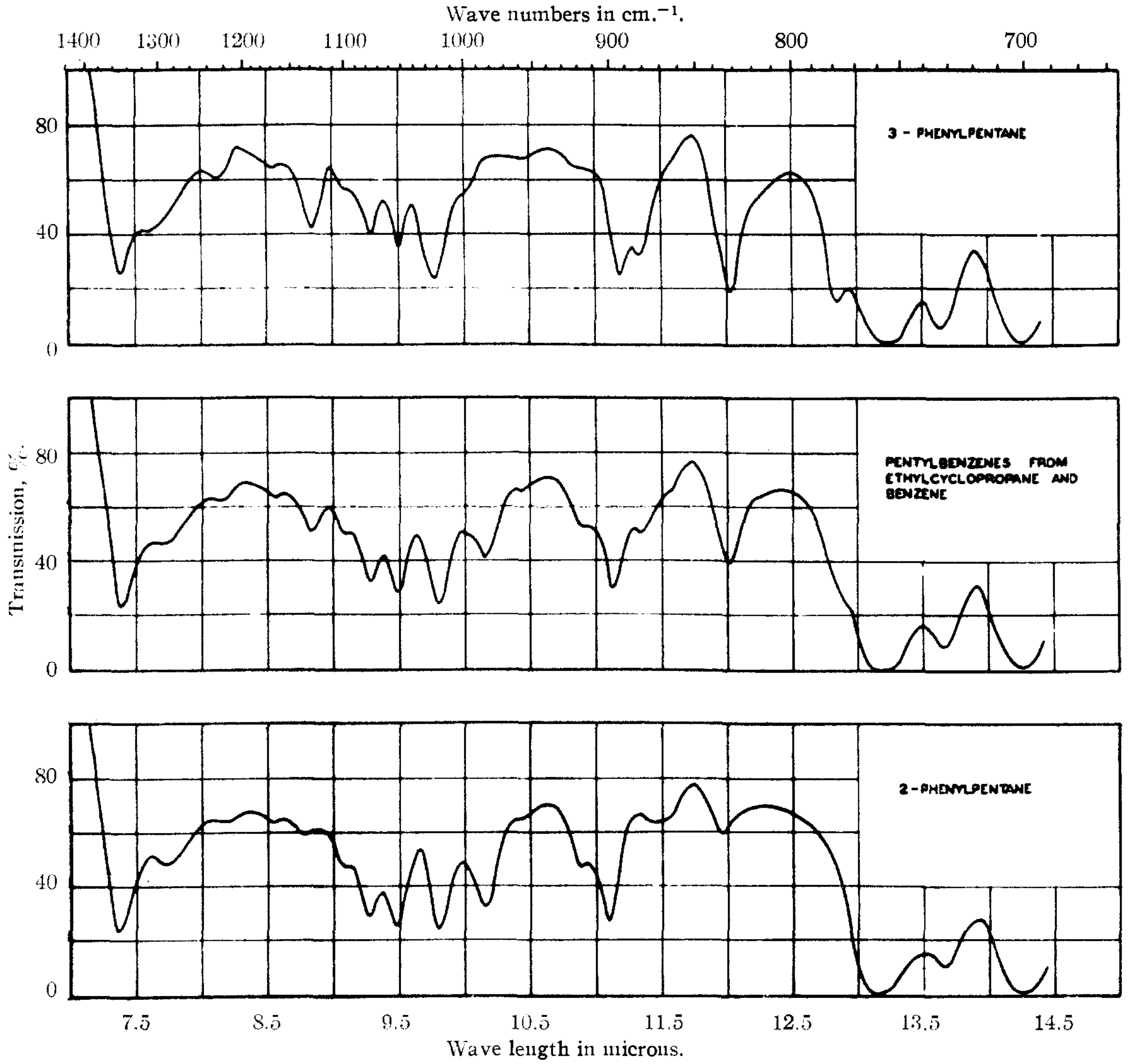
[1] For paper VI of this series, see H. Pines, J. D. LaZerte and V. N. Ipatieff, THIS JOURNAL, **72**, 2850 (1950).

[2] (a) Universal Oil Products Predoctoral Fellow, 1947–1950. (b) Abstracted from the dissertation submitted to the Department of Chemistry, Northwestern University, in partial fulfillment of requirements for the degree of Doctor of Philosophy in August, 1950. Presented in part before the Organic Division, American Chemical Society, Chicago, Ill., September, 1950.

[3] J. H. Simons, S. Archer and E. Adams, THIS JOURNAL, **60**, 2955 (1930).

[4] (a) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); (b) A. V. Grosse and V. N. Ipatieff, *ibid.*, **2**, 447 (1947).

[5] V. N. Ipatieff, H. Pines and B. B. Corson, THIS JOURNAL, **60**, 577 (1938).



Cell thickness: 0.1 mm. Temperature: 25°.

Fig. 1.

first three instances is surprising, because it is well known that isomerizations of the type that would give isopropylbenzene occur very readily under these conditions.

This study has been extended to the reaction of benzene with methylcyclopropane, ethylcyclopropane, 1,1-dimethylcyclopropane and 1,2-dimethylcyclopropane.

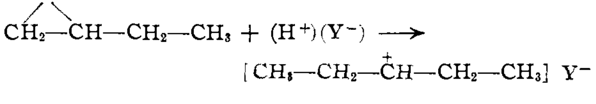
Discussion of Results

Cyclopropane.—In the study of the reaction of cyclopropane and benzene, previous workers[3,4,5] relied on physical constants and solid derivatives for the identification of the propylbenzene obtained. Their findings have been confirmed using infrared spectral analysis; the propylbenzene fraction contained over 98% of *n*-propylbenzene; less than 1%, if any, isopropylbenzene was present.

Methylcyclopropane.—The reaction of methylcyclopropane with benzene catalyzed by hydrogen fluoride gave pure *s*-butylbenzene as determined by infrared spectral analysis. The complete absence of detectable amounts of the other isomeric butylbenzenes, that could conceivably be formed by cleavage of the cyclopropane ring in different directions is indeed interesting.

Ethylcyclopropane.—The reaction of benzene with ethylcyclopropane catalyzed by either hydrogen fluoride, aluminum chloride or sulfuric acid at 0–12° yielded a mixture of amylbenzenes which was identical in all three cases, and consisted of approximately 63% 2-phenylpentane and 37% 3-phenylpentane according to infrared analysis (Fig. 1). Calculations were made at 10.16, 12.02 and 12.84 microns. Treatment of 3-phenylpentane with hydrogen fluoride at 0° gave no reaction, thus demonstrating that the 2-phenylpentane was not formed by the isomerization of 3-phenylpentane. Comparison of infrared spectra showed no detectable amounts of 1-phenyl-2-methylbutane or *n*-amylbenzene (Figs. 2 and 3).

The reaction of ethylcyclopropane with benzene can be represented as



$$\overset{CH_2}{CH_2{-}CH}{-}CH_2{-}CH_3 + (H^+)(Y^-) \longrightarrow [CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_2{-}CH_3]\ Y^-$$

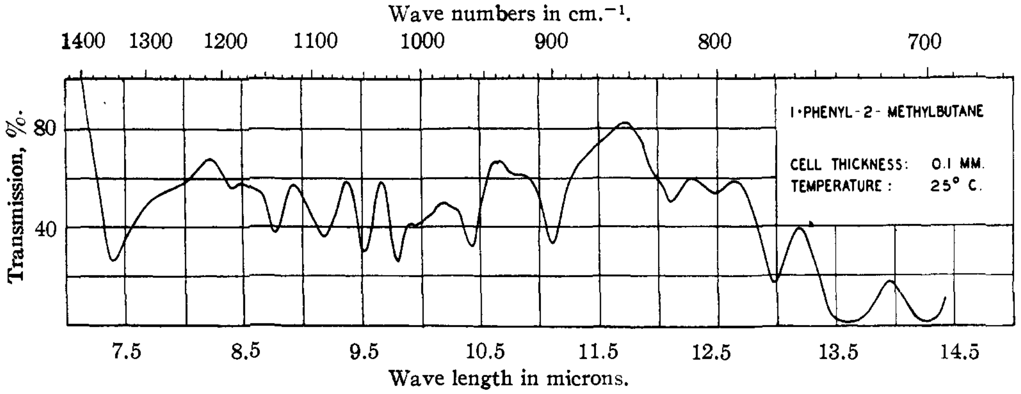


Fig. 2.

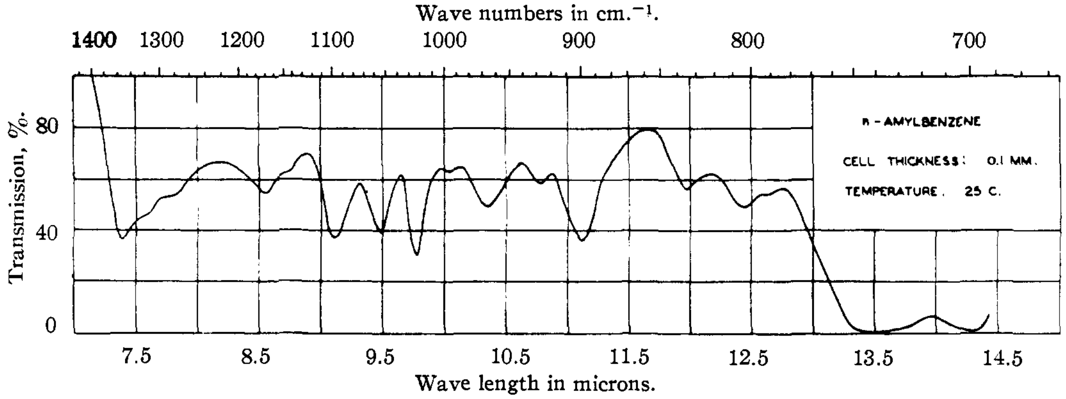
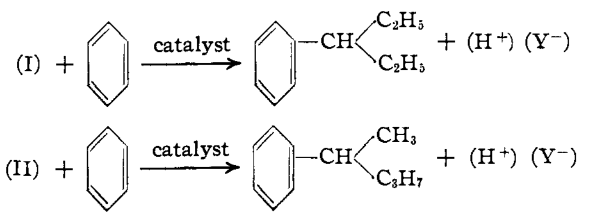


Fig. 3.

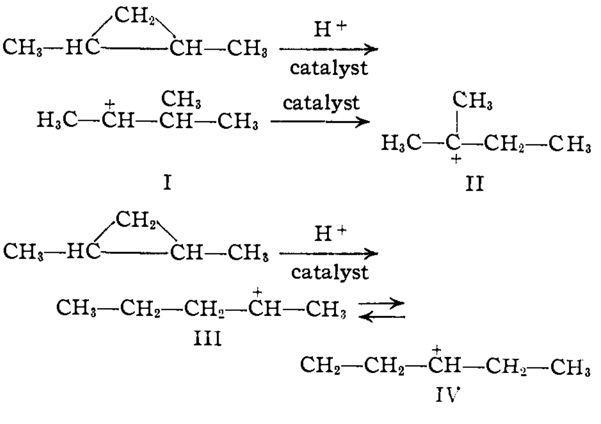
$$\mathrm{I} \xrightarrow{\text{H: Shift}} [CH_3—CH_2—CH_2—\overset{+}{C}H—CH_3]Y^-$$



1,1-Dimethylcyclopropane.—The monoalkylated product from the reaction of benzene with 1,1-dimethylcyclopropane in the presence of hydrogen fluoride consisted of essentially pure *t*-amylbenzene. The infrared spectrum of the alkylation product corresponded with that of pure *t*-amylbenzene with the exception of a small absorption peak in the spectrum of the alkylate. This is probably due to the presence of a trace of some impurity (Fig. 4).

1,2-Dimethylcyclopropane.—The alkylation of benzene with a mixture of *cis*- and *trans*-1,2-dimethylcyclopropane in the presence of hydrogen fluoride as a catalyst gave a mixture consisting, according to infrared absorption spectra of about 83–87% of *t*-amylbenzene, 10–14% of 2- and 3-phenylpentane and 3–5% of 2-phenyl-3-methylbutane (Figs. 4, 5 and 6). Unsuccessful attempts were made to separate this mixture by careful fractionation and also by chromatographing the mixture of 2,4-dinitrophenylhydrazones of the acetyl derivative.

The scission of the cyclopropane ring during the reaction of 1,2-dimethylcyclopropane with benzene may proceed as



t-Amylbenzene would be formed by the isomerization of (I) to (II) and the reaction of the latter with benzene. The other pentylbenzenes present in the reaction mixture would be formed through the reaction of (I), (III) or (IV) with benzene.

Conventional methods were used for the synthesis of the amylbenzenes whose infrared spectra are reported here. The derivatives of acetylated pentylbenzenes are given in Table I; they were prepared according to the procedure described previously.[6]

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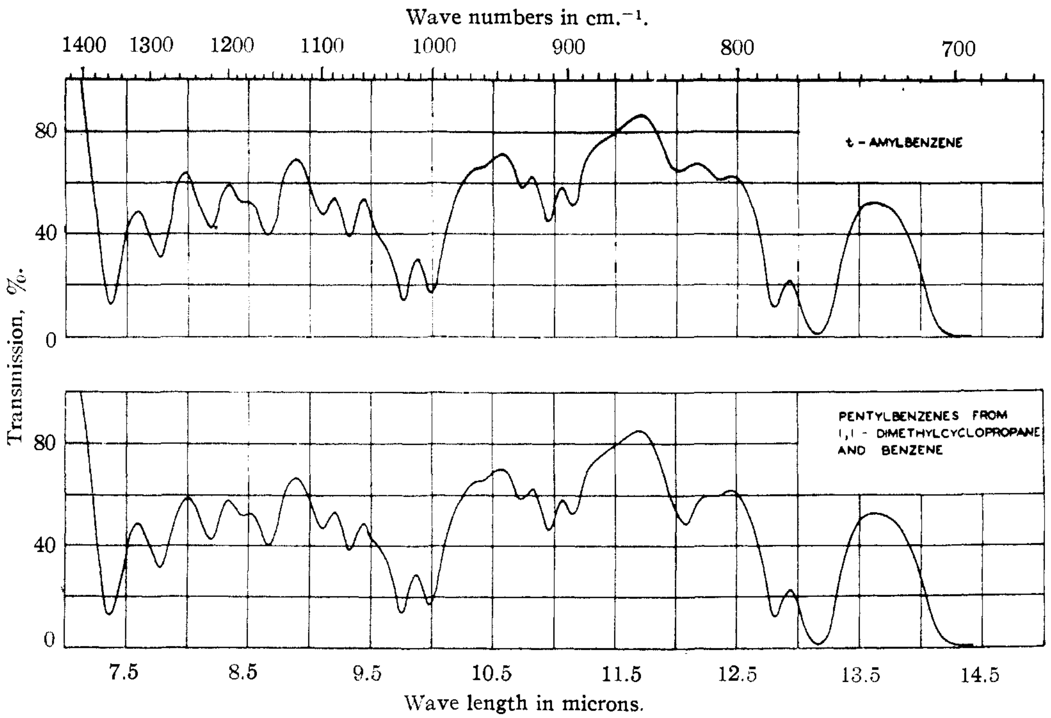
(6) H. Pines, A. Weizmann and V. N. Ipatieff, THIS JOURNAL, **70**, 3859 (1948).



Cell thickness: 0.1 mm. Temperature: 25°.

Fig. 4.

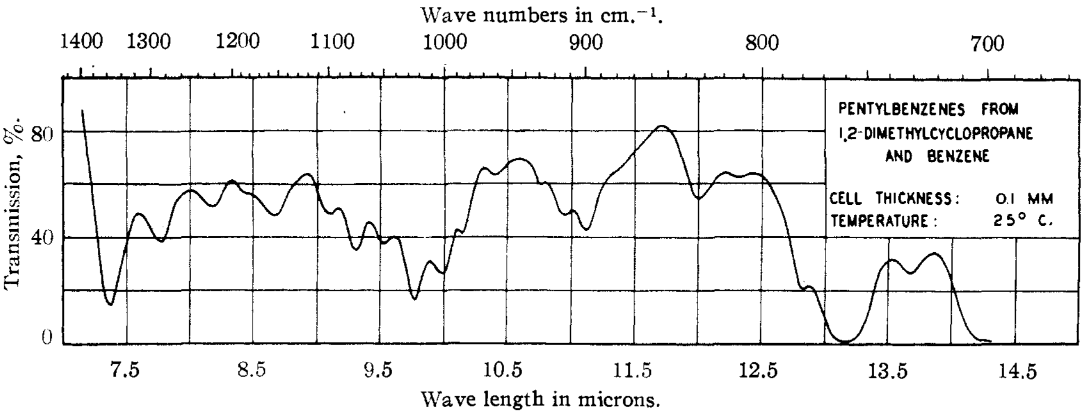


Fig. 5.

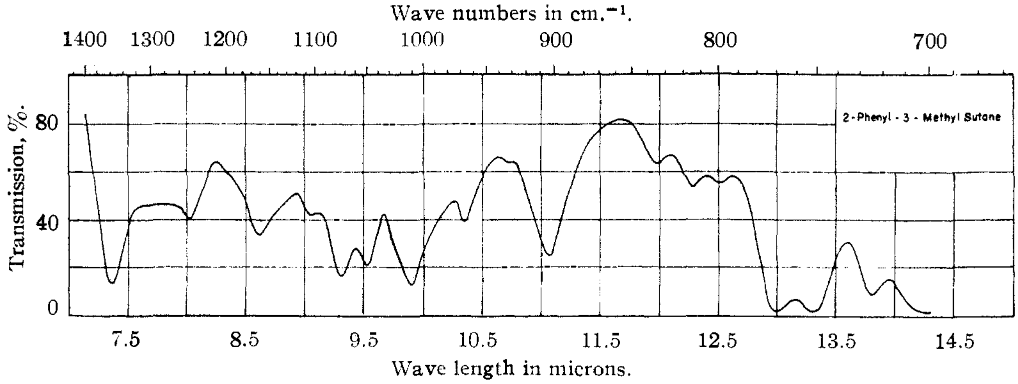


Fig. 6.—Cell thickness: 0.1 mm. Temperature: 25°.

Experimental

A. **Starting Materials.** 1. **Methylcyclopropane** was prepared from 1,3-dibromobutane by means of the Gustavson reaction.[7]

2. **Ethylcyclopropane.**—Methyl cyclopropyl ketone[8] was reduced in 55% yield to ethylcyclopropane by the modified Wolff–Kishner method as described by Huang-Minlon.[9] Thirty-eight grams of ethylcyclopropane, b.p. 35.5–35.6°, n^{20}D 1.3775 were obtained from the reaction of 84 g. of methyl cyclopropyl ketone, 100 cc. of 85% hydrazine hydrate and 80 g. of potassium hydroxide in 600 cc. of diethylene glycol.

TABLE I

DERIVATIVES OF ACETYLATED AMYLBENZENES

	2,4-Dinitrophenylhydrazone		Semicarbazone	
	M.p., °C.	Anal.[a] nitrogen, %	M.p., °C.	Anal.[b] nitrogen, %
2-Phenylpentane	149–149.5	15.09	172.5–173.5[c]	...
1-Phenyl-2-methylbutane	147–148	15.07	196.5–197	17.36
n-Amylbenzene	152.5–153	...	181–181.5[d]	...
3-Phenylpentane	155.5–156.5	15.44	164.5–165	17.28

[a] Calcd. for $C_{19}H_{22}N_4O_4$: N, 15.13. [b] Calcd. for $C_{14}H_{21}N_3O$: N, 17.00. [c] G. F. Hennion and S. F. deC. McLeese, THIS JOURNAL, **64**, 2421 (1942), give m.p. 173–174°. [d] A. Zaki and H. Fahim, *J. Chem. Soc.*, 307 (1942), give m.p. 180–181°.

3. **1,1-Dimethylcyclopropane** was prepared in about 30% over-all yield by the method described in the literature.[10]

4. **1,2-Dimethylcyclopropane** was prepared from 2,4-dibromopentane by means of the Gustavson reaction.[7,11] Precise fractionation showed the products to consist of two components, b.p. 27.5 and 35.4°. These are probably *cis-trans* isomers. The product was stable to 2% permanganate at 0°.

B. **Alkylation Experiments.** 1. **Ethylcyclopropane. Hydrogen Fluoride Catalyst.**—The general procedure used was the same as described previously.[12] The reaction of 7.0 g. (0.1 mole) of ethylcyclopropane with 94 g. (1.2 moles) of benzene in the presence of 10 g. (0.5 mole) of hydrogen fluoride at 0–5° gave 6.1 g. (41%) of monoalkylated material, b.p. 64–65° (5 mm.), n^{20}D 1.4870 and 3 g. of high-boiling residue, probably polyalkylated products. The *p*-acetamino- and *p*-benzamino- derivatives[13] were prepared, but repeated crystallization failed to give a melting point corresponding to one of the pure amylbenzenes. The infrared spectra shown in Fig. 1 indicate that the mixture consists of about 63% of 2- and 37% of 3-phenylpentane.

Aluminum Chloride Catalyst.—The general procedure described in the literature for aluminum chloride-catalyzed alkylations was followed.[12] From the reaction of 17.5 g. (0.25 mole) of ethylcyclopropane, and 78 g. (1.0 mole) of benzene in the presence of 12 g. (0.1 mole) of aluminum chloride at 5–12° (hydrogen chloride was frequently passed through the mixture) there was obtained 18.8 g. (50.5%) of monoalkylated product, b.p. 191–192°, n^{20}D 1.4870 and 8 g. of high-boiling residue. The infrared absorption spectrum of the monoalkylated material was identical with that of the product from the hydrogen fluoride-catalyzed reaction.

Sulfuric Acid Catalyst.—The general procedure described in the literature for sulfuric acid-catalyzed alkylations[13] was followed. The reaction of 16.8 g. (0.24 mole) of ethylcyclopropane with 78 g. (1.0 mole) of benzene in the presence of 20 ml. of 96% sulfuric acid at 5–10° gave 16.5 g. (46.5%) of monoalkylated product, b.p. 189.5–191.5°, $n^{19.5}$D 1.4880. The residue (4.5 g.) was a brown viscous oil. The infrared spectrum of the monoalkylated product was identical with that obtained from the hydrogen fluoride and sulfuric acid catalyzed reactions.

2. **1,1-Dimethylcyclopropane.**—Five grams (48%) of *t*-amylbenzene, b.p. 189–191°, n^{20}D 1.4946, was obtained from the reaction of 4.7 g. (0.07 mole) of 1,1-dimethylcyclopropane and 62 g. (0.8 mole) of benzene in the presence of 7 g. (0.34 mole) of hydrogen fluoride at 0–5°. The infrared spectrum of this product is shown in Fig. 3. One-half cc. of this product was acetylated[6] and the 2,4-dinitrophenylhydrazone of the acetyl derivative prepared. It melted at 177–177.5° and showed no depression when mixed with the corresponding derivative of an authentic sample of pure *t*-amylbenzene.[14]

3. **1,2-Dimethylcyclopropane.**—Eleven grams (0.16 mole) of 1,2-dimethylcyclopropane (mixture of low- and high-boiling fractions) and 146 g. (1.86 moles) of benzene in the presence of 18 g. (0.9 mole) of hydrogen fluoride at 0–5° gave 10.8 g. (42.5%) of monoalkylated product, b.p. 188–189°, n^{20}D 1.4920–1.4923, and 6.6 g. of residue. Careful fractionation of the monoalkylated product through a Piros–Glover micro column rated at about 50–60 theoretical plates failed to give any appreciable separation; furthermore, attempts to separate the mixture of 2,4-dinitrophenylhydrazones of the acetyl derivative by chromatography over activated alumina resulted in failure. The infrared spectrum of the monoalkylate, which is shown in Fig. 4, indicates the presence 83–87% of *t*-amylbenzene and 10–14% of a mixture of 2- and 3-phenylpentane, and 2–3% of 2-phenyl-3-methylbutane.

4. **Cyclopropane.**—The general procedure of Simons and co-workers[3] was followed. From approximately 2.5 liters (0.1 mole) (gas, 28°, 750 mm.) of cyclopropane, 186 g. (2.4 moles) of benzene and 10 g. (0.5 mole) of hydrogen fluoride there was obtained 3.4 g. (29%) of monoalkylated product, b.p. 150–158°, n^{20}D 1.4907, and 0.7 g. of yellow, viscous residue. The infrared spectrum of the monoalkylated product showed it to be *n*-propylbenzene.

5. **Methylcyclopropane.**—The reaction of benzene, 78 g. (1.0 mole) with methylcyclopropane, 11.2 g. (0.2 mole), in the presence of hydrogen fluoride, 20 g. (1.0 mole), at 0–5° gave 13.0 g. (48% yield) of monoalkylated product, b.p. 170.5–171.5°, n^{20}D 1.4896. Infrared spectral analysis showed this product to be pure *s*-butylbenzene.

C. **The Reaction of 3-Phenylpentane with Hydrogen Fluoride.**—A solution of 7 g. (0.05 mole) of 3-phenylpentane in 78 g. (1.0 mole) of benzene was treated with 10 g. (0.5 mole) of hydrogen fluoride at 0–5° for 40 minutes. The reaction mixture was worked up in the usual manner and comparison of infrared spectra showed it to be identical with the starting material.

D. **Synthesis of Pentylbenzenes.**—The pentylbenzenes were synthesized by methods that have been reported in the literature. The appropriate carbinols, synthesized by the Grignard reaction, were dehydrated over activated alumina at 330–350°, and the resulting olefins were selectively hydrogenated at 50°, under 100 atmospheres hydrogen pressure in the presence of nickel–Kieselguhr using an equal volume of pentane as a solvent. Under these conditions the aromatic ring is not hydrogenated. The products were fractionated through a wire spiral packed column rated at five plates and center cuts were used for the spectra reported here. The constants of the hydrocarbons thus obtained checked with those reported in the literature.[15]

A Beckman model IR2 spectrophotometer was used to obtain the infrared spectra. The cell thickness was 0.1 mm. in each case, and carbon disulfide in a matched cell was used as the blank.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 5, 1951

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[7] G. Gustavson, *J. prakt. Chem.*, **36**, 300 (1887).

[8] Obtained from U. S. Industrial Chemicals.

[9] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[10] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

[11] N. D. Zelinsky and M. N. Ujedinoff, *J. prakt. Chem.*, [2] **84**, 543 (1911).

[12] H. Pines, A. Edeleanu and V. N. Ipatieff, *ibid.*, **67**, 2193 (1945).

[13] V. N. Ipatieff and L. Schmerling, *ibid.*, **59**, 1056 (1937); **60**, 1476 (1938).

[14] Furnished by Universal Oil Products Company.

[15] A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).