precisely. These mixtures were prepared of 4-picoline:3-picoline:2-picoline, namely, 0:10:90, 2:8:90 and 5:5:90%. The 4-picoline was detectable as a shoulder at 8.20 μ (run against rock salt) on the 8.1 μ bands of the other picolines, and semi-quantitatively estimated in unknowns by comparison with these standard curves. If 5% or more of 4-picoline was present, then a peak at 9.3 μ appeared under these conditions from which a calibration could be set up, but in our mixtures the quantity was always less than 5%.

If the concentration of 3-picoline is very high then the band for 4-picoline at 8.20 μ does not appear below concentrations of 5% for the latter. The only band suitable for analysis is 10.0 μ but 2-picoline interferes with it if it is present in amounts of more than a few per cent.

Identification of Naphthalene, Quinoline, Benzonitrile.—Naphthalene was isolated as such from the pyrolytic products of toluene; m.p. 76–78°, mixture m.p. 78–80° with known naphthalene of m.p. 80°. The infrared method was developed for analyzing small quantities of naphthalene admixed with biphenyl. Various solutions of 2 M concentration in carbon tetrachloride were run against pure carbon tetrachloride in the solvent cell. Naphthalene was detectable by peaks at 8.81 and 10.40 μ. These values were obtained using the peak at 10.40 μ (mole $C_{10}H_8$, moles Ph_2, log I_0/I): 0.0, 2.0, 0.000; 0.2, 1.8, 0.026; 0.5, 1.5, 0.112; 1.0, 1.0, 0.247.

Quinoline was collected in a complex fraction at 40–70° (0.04 mm.) and its presence demonstrated by picrate formation and by infrared. The picrate was washed several times with absolute ether; m.p. 196–200°, mixed m.p. 195–197° with that of pure quinolinium picrate of m.p. 197–200°. The infrared spectrum was taken and peaks were noted which matched those of pure quinoline. Then 1 drop of pure quinoline was added to 10 drops of the fraction and the spectrum was retaken on the same graph paper. No new peaks appeared and over 30 of the quinoline peaks were intensified.

Benzonitrile was present in the quinoline fraction. Its sharp infrared band at 4.42 μ was characteristic. Diluting 10 drops of this fraction with 1 drop of benzonitrile caused no new peaks to appear, but it intensified all of the benzonitrile peaks. A sample containing only benzonitrile and quinoline was analyzable for both components by the infrared method using rock salt in the solvent well. The 4.42 μ band was used for benzonitrile and the 8.88 μ band for quinoline. Table VI gives the data.

TABLE VI

ANALYSIS OF BENZONITRILE–QUINOLINE MIXTURES

Weight, g.		log I_0/I at	
PhCN	C_9H_7N	8.88 μ	4.42 μ
72	28	1.641	0.576
32	68	0.755	1.136

Methylpyrazine.—The 3-step synthesis of Jones[18] was modified in the last step. Our yields of 2-methylquinoxaline in the first step from *o*-phenylenediamine and acrolein were 80–90%. We obtained a lower yield (35 instead of 71%) of 5-methyl-2,3-pyrazinedicarboxylic acid in the oxidation step, but we made no attempt to improve it. Jones decarboxylated the latter in an autoclave (presumably because of sublimation difficulties at temperatures above 200° which must be used), but we found it simpler to use a flow method through our tube furnace. The diacid was heated in a small flask attached to a tube extending upward through the furnace, which was held at 250°. Vapors from the top of the tube were condensed (yellow condensate) and redistilled; b.p. 131.5–133.5°. The yield of 42% was lower than Jones's (63%),but no doubt it too could be improved with more study. A small amount of monoacid crystals collected at the top of the tube. The picrate of our methylpyrazine melted at 131–132° (literature[19] 133°). These peaks were found in the infrared spectrum of the methylpyrazine and the peaks are strong unless indicated medium (m) or weak (w): 2.82m, 3.3, 3.8w, 4.1w, 4.4w, 4.7w, 4.8w, 5.1m, 5.6m, 6.0m, 6.28, 6.50, 6.8–7.2, 7.64, 7.96, 8.5–8.6, 9.4–9.8, 10.20, 11.9–12.1, 12.6m, 13.28, 15.8 mμ.

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[19] C. Paal and C. Koch, *Ber.*, **37**, 4383 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Pyrolytic Formation of Arenes. IV. Pyrolysis of Benzene, Toluene and Radioactive Toluene

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Toluene-α-^{14}C, on decomposition at 825°, gave rise to benzene, naphthalene, phenanthrene and other products. The benzene was 3.2% as radioactive as the original toluene, showing that not all of it could have come by simple scission of the methyl group. The naphthalene was 17.6% as radioactive. Both the phenanthrene and anthracene were nearly twice as radioactive as the starting toluene. Infrared analysis confirmed the fact that naphthalene was not a pyrolytic product of benzene.

Before studying isotopically-labeled toluene, ordinary toluene was first studied. In two runs at 825° there was recovered 39% and 28% of the toluene at 10 and 13 seconds contact time, respectively. About 10 mole % of benzene was formed in each run. The tarry residues of the two runs were combined and processed for solid products. Naphthalene was isolated as such by vacuum distillation and was identified by undepressed melting point with authentic naphthalene.

The residual tar, after treating with maleic anhydride to tie up reactive dienes (as anthracene), was placed on an alumina column. The phenanthrene was eluted therefrom with hexane and was identified both by mixture m.p. and by conversion to its picrate. Other components of the tar were not investigated. In the subsequent work benzene, naphthalene, phenanthrene and anthracene all were isolated from the radioactive toluene.

These runs were duplicated by Miss J. I. Simon who isolated 1.7 mole % of naphthalene and 45–58 weight % of higher boiling substances. Since C_2-hydrocarbons never had been sought for in the gaseous products prepared in this manner (825°, atmospheric pressure, 10 sec. contact time) the gas was collected and analyzed. Of the 45 mole % of gas formed, 1.2 mole % was ethylene and 0.0% was acetylene. Obviously, acetylene can play no significant role in the reaction mechanism. Others who have analyzed the gases from toluene used different conditions. Szwarc's conditions[2] involved low pressure. Mrs. Ingold[3] analyzed

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[1] Abbott Fellow, summer 1958; United States Rubber Company Foundation Fellow, 1958–1959.

[2] M. Szwarc and C. Leigh, *J. Chem. Phys.*, **20**, 403, 844 (1952).

[3] K. U. Ingold and F. P. Lossing, *Can. J. Chem.*, **31**, 30 (1953).

gaseous products from toluene by the mass spectrograph, but her reaction temperatures were 1350–1450°.

Miss Simon's study also included pyrolysis of benzene at 825 and 850° (11 sec.) to search for possible naphthalene. The yields of biphenyl ranged between 16–23 mole %. Any naphthalene in the products should have appeared in the first biphenyl to distil under reduced pressure. This first fraction was, however, pure biphenyl. Absence of peaks in the infrared spectra at 8.81 or 10.40 μ, where naphthalene absorbs strongly, demonstrated that naphthalene was not formed in identifiable amounts. Synthetic mixtures of biphenyl and naphthalene showed that naphthalene in less than 5% concentration was readily detectable in this way.

In a recent paper, Badger and Novotny[4] reported on their pyrolysis of benzene. As would be expected, the chief products were biphenyl and terphenyl; but also separated in trace amounts by chromatography and identified by ultraviolet spectra were triphenylene (0.67%), anthracene (0.13), chrysene (0.13), phenanthrene (0.10), fluorene (0.08) and 3,5-benzofluoranthene (0.05).

In the first paper[5] it was pointed out that the benzene formed by pyrolyzing toluene could come in either of two ways: (1) initial scission into benzyl radical and hydrogen atom, followed by interaction of the latter with toluene to yield benzene and a methyl radical. (2) Scission as before into benzyl, the latter cleaving into the propargyl–propadienyl fragment (Ia) with subsequent rearrangement into trimethine (Ib) and dimerization to benzene.

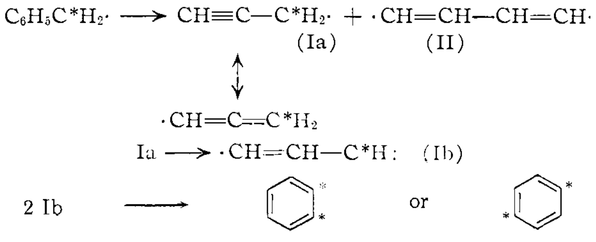
It seemed possible to test these assumptions by means of an isotopically labeled methyl group in the toluene. The first pathway would give rise to benzene devoid of radioactivity (let $^{14}C = C^*$),

$$C_6H_5C^*H_3 \longrightarrow C_6H_5C^*H_2\cdot + H\cdot$$

$$C_6H_5C^*H_3 + H\cdot \longrightarrow C_6H_6 + C^*H_4$$

The second pathway would yield benzene with twice the radioactivity of the original toluene.

$$C_6H_5C^*H_3 \longrightarrow C_6H_5C^*H_2\cdot + H\cdot$$



$$C_6H_5C^*H_2\cdot \longrightarrow \underset{(Ia)}{CH{\equiv}C{-}C^*H_2\cdot} + \underset{(II)}{\cdot CH{=}CH{-}CH{=}CH\cdot}$$

$$\updownarrow$$

$$\cdot CH{=}C{=}C^*H_2$$

$$Ia \longrightarrow \cdot CH{=}CH{-}C^*H: \quad (Ib)$$

2 Ib ⟶ or

Accordingly, toluene-α-^{14}C was studied.

Wheland and Schwartz's[6] method of synthesis was chosen, although no experimental details were listed in their "letter"

$$C^*O_2 \longrightarrow PhC^*OOH \xrightarrow{LiAlH_4} PhC^*H_2OH \xrightarrow[Pd-C]{H_2} PhC^*H_3.$$

A later, similar synthesis[7] converted the benzoic acid into its methyl ester before reduction with $LiAlH_4$ and used amalgamated zinc plus HCl in the reductive cleavage of benzyl alcohol to toluene. The stated yield in this last step from benzyl alcohol was 44%. In contrast, we obtained a 50% over-all yield of toluene from benzoic acid. To ensure that all of the radioactivity in our toluene was in the methyl group, we oxidized the compound to benzoic acid and decarboxylated the latter. The resulting benzene had no radioactivity.

This active toluene, appropriately diluted with ordinary toluene, was pyrolyzed at 825° and 24 sec. contact time. The relatively long duration of heating was purposely chosen to ensure a higher extent of decomposition. In consequence, only 4% was recovered. Benzene, obtained on fractionation of the product, represented a 17 mole % yield, leaving a 47 weight % of tar residue from which naphthalene, phenanthrene and anthracene were separated in turn by chromatography on silica gel. All three of the solid hydrocarbons were crystallized to purity from alcohol before measuring their radioactivities.

The activity of the toluene charge stock was 1.32 μc./mmole. That of the product benzene was 0.0427 μc./mmole, of naphthalene 0.232 μc., of phenanthrene 2.26 μc., and of anthracene 2.52 μc. Thus, the relative number of labeled carbon atoms per molecule in benzene was 0.032 (*i.e.*, it was 3.2% as active as the original toluene), the naphthalene 0.176, the phenanthrene 1.71, and the anthracene 1.91.

That the benzene fraction was indeed radioactive *per se* and not because of any contamination with toluene was demonstrated by means of its infrared spectrum. The latter was in all respects superimposable on the spectrum of pure benzene. It had no absorption peak at 13.62 μ. It was established that a solution containing 1% of toluene in benzene could be detected easily by appearance of this peak.

Since the benzene was 3.2% as active as the toluene charge stock, and since each molecule of radioactive benzene must contain two ^{14}C atoms, it is evident that 1.6% of the toluene decomposed according to pathway 2, above, making use of trimethine (Ib) fragments. The mechanisms covering this, as well as the formation of naphthalene, anthracene and phenanthrene, have been presented[5] in paper I.

Since completion of this work an interesting paper has appeared[8] covering the pyrolysis at 700° of isotopically labeled ethylbenzene, $C_6H_5-{}^{14}CH_2-CH_3$. The products and their relative number of labeled carbon atoms per molecule were: toluene, 0.74; benzene, 0.024; styrene, 1.07; naphthalene, 2.00; biphenyl, 0.045; phenanthrene, 1.05; anthracene, 1.03; pyrene, 2.4, 2.65; chrysene, 3.14; 3,4-benzofluoranthrene, 0.91.

These workers postulated initial scission into $PhC^*H_2\cdot + CH_3\cdot$ and into $Ph\cdot + CH_3C^*H_2\cdot$. Since their benzene was only 2.4% as radioactive as the ethylbenzene they regarded it as "practically

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[4] G. M. Badger and J. Novotny, *J. Chem. Soc.*, 3400 (1961).

[5] C. D. Hurd, A. R. Macon, J. Simon and R. Levetan, *J. Am. Chem. Soc.*, **84**, 4509 (1962).

[6] G. W. Wheland and J. R. Schwartz, *J. Chem. Phys.*, **17**, 425 (1949).

[7] L. Kendrick, Jr., B. Benjamin and C. Collins, *J. Am. Chem. Soc.*, **80**, 4057 (1958).

[8] G. W. Badger and R. W. L. Kimber, *J. Chem. Soc.*, 3407 (1961).

inactive." It is striking, however, that their 2.4% is of the same order of magnitude as our 3.2%. Our larger value may reflect our higher temperature. They did not discuss breakdown of the benzyl radical but they did mention that any breakdown (into C_2- or C_4-units) and resynthesis of the benzene ring "must occur only to a very small extent at 700°." From our results, it seems reasonable to infer that their radioactive benzyl radical decomposed in part into fragments Ia or Ib to generate the radioactive benzene which was noted.

Their radioactivities for naphthalene, phenanthrene and anthracene differed markedly from ours, but this might be expected in view of the differing source materials. The authors postulated radicals and olefins as intermediates (*e.g.*, phenanthrene *via* styrene + phenyl, or naphthalene *via* phenethyl + ethylene) but since styrene, ethylene or the phenethyl radical were not products of our work with toluene no extended discussion of it seems warranted in this paper.

Experimental

Toluene.—The toluene employed was dried for 2 days over sodium, then was distilled through a short Vigreux column; b.p. 109–110°. The distilled product had an infrared spectrum identical with that of toluene found in tables of the American Petroleum Institute.

Toluene-α-^{14}C.—The benzoic acid was made from phenylmagnesium bromide and $^{14}CO_2$ by standard vacuum techniques.[9]

A mixture of 5.9535 g. of $BaCO_3$ and 0.0647 g. (5 millicuries) of $Ba^{14}CO_3$ was used to generate $^{14}CO_2$ for carbonation of a solution of 0.035 mole (by titration) of phenylmagnesium bromide in 43 ml. of anhydrous ether. During the processing, 4.3352 g. of inactive benzoic acid was added as a scavenger. The total yield of benzoic-α-^{14}*C* acid was 6.5875 g.

This total acid was dissolved in 75 ml. of dry ether and added dropwise during an hour into a stirred solution of 3.9 g. of lithium aluminum hydride in 75 ml. of dry ether. After 30 min. more, 100 ml. of moist ether was added cautiously, after which 100 ml. of 10% sulfuric acid. The mixture was stirred for several hours, the ether layer was separated, and the aqueous layer was extracted 5 times with 100-ml. portions of ether. The combined ether layers were dried (Na_2SO_4) and evaporated.

The residue of benzyl-α-^{14}*C* alcohol was diluted with 5 ml. of ordinary benzyl alcohol and then with enough 95% ethanol to make 50 ml. It was reduced at 3 atm. hydrogen pressure in a Parr apparatus, using 2 g. of 10% Pd–C catalyst. When hydrogen was no longer absorbed, 300 ml. of saturated salt solution was added. The toluene layer was separated, the aqueous layer ether extracted, the combined non-aqueous layers dried and distilled. The toluene-α-^{14}*C* (2.47 g., b.p. 108–110°) thus obtained was diluted to 30 ml. with ordinary toluene. The infrared spectrum of this mixture was identical to that of pure toluene.

The radioactivity of this hydrocarbon was determined on a sample by further 10-fold dilution with ordinary toluene, the whole oxidized to carbon dioxide, and its radioactivity measured in a Dynacon Electrometer, model 6000, made by Nuclear-Chicago Corporation. The toluene-α-^{14}*C* (the 30 ml. of product) was found to have an activity of 1.32 μ c./mmole.

Location of Radioactivity in the Toluene.—A sample (2.5 g.) of radioactive toluene, diluted 10 times, was oxidized to benzoic acid (2.05 g., 62% yield) with hot aqueous alkaline potassium permanganate by the procedure of Mitchell.[10] To decarboxylate the benzoic acid, 0.359 g. of it was placed in a side-arm tube with an excess (1.0 g.) of cupric oxide and 10 ml. of quinoline. The side-arm delivered into a cold trap at −78° to condense benzene and then into an absorber for CO_2 containing an aqueous solution of carbonate-free sodium hydroxide. A slow stream of nitrogen was passed through the system, then the tube was heated ultimately to 265° for 3 hours. The nitrogen stream was shut off between the bath temperature of 100 to 200°. The collected benzene was purified by the method of Pines and Shaw[11]; yield, 0.163 g. (71%). Its radioactivity was determined by combustion to carbon dioxide and measuring the latter (in the manner described below for the sodium carbonate product). This carbon dioxide had no activity, hence the six carbons of the ring had no activity.

To determine the side chain activity the sodium carbonate in the alkaline solution of the CO_2-absorber was treated with ammonium chloride (in boiling water). Then barium chloride (in boiling water) was added with swirling, and the flask was evacuated until the hot water boiled. The stopcock to the pump then was closed. After 15 minutes the barium carbonate was collected on a filter, rinsed with hot water and acetone, and dried at 110° for 15 min. A weighed sample of this salt was placed in an apparatus to be treated with 10 ml. of concd. sulfuric acid, heated to boiling, to generate carbon dioxide. This gas was passed into an ionization chamber. Its activity was measured and found to be 0.124 μc./mmole.

Pyrolysis.—Both ordinary toluene and the toluene-α-^{14}*C* sample were pyrolyzed making use of previously described procedures.[12] From the 25 ml. of toluene-α-^{14}*C* (1.32 μc./mmole), heated at 825° during 128 minutes (hot contact time, 24 sec.) there was collected 3350 ml. of gas and 13.65 g. of black liquid as products. The latter was fractionated through a Davis column: 78–80°, 2.633 g.; 80–82°, 0.368 g.; 82–109°, 0.891 g. Absence of toluene in the 78–80° cut was certified by no infrared peak at 13.62 μ and by complete identity of the spectrum with that of pure benzene. A known mixture of 1% toluene in benzene showed the 13.62-μ absorption unmistakably. Two determinations of radioactivity of this benzene gave values of 0.0436, 0.0419 μ c./mmole, or an average of 0.0427. This is 3.2% of the starting activity.

The residue from the distillation was placed on an alumina column (3 × 70 cm.) and eluted therefrom without separation of fractions with 1100 ml. of petroleum hexane, then with 440 ml. of chloroform. The combined solution was concentrated to 25 ml. and separated into fractions by chromatographing through a second 3 × 70 cm. alumina column, using petroleum hexane as eluent. Each 100 ml. of eluent was processed: fractions 1–5, no solids; 6–7, naphthalene; 8–9, a few yellow crystals; 10–11, phenanthrene; 12–14, an orange oil; 15–19, anthracene; 20–23, trace of orange oil; 24–29, gold-colored solid, 25 mg.

Naphthalene was recrystallized from 95% ethanol; m.p. 69–75°. It was converted to its picrate (m.p. 148–149°) to remove any biphenyl. The picrate was placed on a column of silica gel (1.8 × 26 cm.) through which naphthalene passed readily on elution with hexane. After crystallizing from 95% alcohol, the naphthalene melted at 78–79°, mixed m.p. 79–80°, yield 79.5 mg. Two assays of this naphthalene showed it to have 0.237, 0.227 (av. 0.232) μ c./mmole.

The crude phenanthrene was thrice recrystallized from 95% ethanol to yield 32 mg. of white solid, m.p. 99–100°. Its activity was 2.29, 2.23 (av. 2.26) μ c./mmole.

The crude anthracene was thrice recrystallized from absolute ethanol; yield 98 mg. of an off-white powder, m.p. 210–212°. Its activity was 2.46, 2.58 (av. 2.52) μ c./mmole.

The other chromatographic fractions were not identified, but naphthacene and chrysene are suggested as components of the last fraction in view of the gold color.

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[10] J. J. Mitchell, *J. Am. Chem. Soc.*, **80**, 5848 (1958).

[11] H. Pines and A. Shaw, *ibid.*, **79**, 1474 (1957).

[12] C. D. Hurd, R. V. Levetan and A. R. Macon, *ibid.*, **84**, 4515 (1962); C. D. Hurd and J. I. Simon, *ibid.*, **84**, 4519 (1962).