bon dioxide. The advantage of the sodium carbonate is solubility of sodium sulfate in the concd. sulfuric acid used to generate the carbon dioxide as contrasted with insolubility of the barium sulfate.

After carbonation, the magnesium salt was hydrolyzed by 100 ml. of 6 *N* hydrochloric acid. After processing as for benzoic-α-^{14}C acid,[3] using 1.87 g. of ordinary 2-thenoic acid as scavenger, there was obtained 4.55 g. of 2-thenoic-α-^{14}C acid. This was 75% yield, somewhat lower than the 90% obtained in practice runs with non-radioactive material.

Reduction.—This 4.55 g. of acid was admixed with 1.24 g. of inactive acid: total, 5.79 g. or 0.045 mole. It was dissolved in 100 ml. of dry ether and added dropwise into a stirred slurry of 3.3 g. (2.5 equivalents) of $LiAlH_4$ in 100 ml. of dry ether. After 2 hours of stirring the product was hydrolyzed by cautious addition of saturated ammonium chloride solution. The sandy textured solid was filtered off, rinsed twice with ether, suspended in water and the suspension twice extracted with ether. The filtrate was extracted with four 100-ml. portions of ether. The combined ether extract was dried (Na_2SO_4) and evaporated to 50 ml. in an air stream.

2-Thenyl-α-^{14}C Chloride.—To the above 50 ml. was added 6.4 g. of inactive 2-thenyl alcohol. This, plus the 5.1 g. of alcohol theoretically formed by reduction of the acid, makes 11.5 g. (0.1 mole). To it was added 8.7 g. (0.11 mole) of pyridine. The flask, cooled by ice, was stirred and into it was added during one hour 12.5 g. (0.105 mole) of thionyl chloride in 15 ml. of dry ether. The temperature was held below 15°. Then it was stirred for 4 hours at 0°.

The ether was decanted and the residual white solid was thrice slurried with 50-ml. portions of ether. The solid was then dissolved in water, with evolution of SO_2, and the solution was twice extracted with ether. The combined ether portions were washed with very dilute sodium hydroxide, dried (Na_2SO_4), and concentrated to 200–250 ml.

2-(Methyl-α-^{14}C)-thiophene.—The above ether solution was transferred with adequate rinsing into a flask and to it was added 50 g. of zinc dust and 120 ml. of glacial acetic acid. It was stirred at reflux for 12 hours, then the ether was decanted and the residue was repeatedly stirred with 50-ml. portions of ether. The ether solution, after washing several times with water to remove possible acetic acid, was dried ($CaCl_2$) and concentrated. To the concentrate was added 50 g. of inactive 2-methylthiophene (from The Texas Co.) and the whole was fractionated through a 30-cm. vacum-jacketed Vigreux column. The yield of product boiling over a 0.5° range was 54.5 g.

Prior to assay, a small amount of this radioactive 2-methylthiophene was diluted 11.4 times with ordinary 2-methylthiophene. The activity was found to be 0.111, 0.112 μc./mmole, from which the starting sample was 0.112 × 11.4 or 1.28 μc./mmole.

Pyrolysis.—A 50-ml. sample of this radioactive 2-methylthiophene was pyrolyzed through the Vycor reaction tube at 800° with a hot contact time of 10.5 sec. The non-gaseous product (40.5 g.) collected in the ice trap as a black liquid which was fractionated through a Davis column: b.p., up to 84°, 6.55 g.; 84–109°, 1.27 g.; 109–112°, 12.17 g. The residue (A), 54% by weight, was processed by chromatography (below).

The recovered 2-methylthiophene was 24%. The products isolated were benzene, 1 mole %; thiophene, 19 mole % (by difference); naphthalene, 0.1 mole %; benzothiophene, 0.1 mole %.

Activity of the Benzene.—From 3 g. of the first fraction containing benzene and thiophene was isolated 0.17 g. of *m*-dinitrobenzene, using the procedure outlined above. It was recrystallized 3 times from methanol; m.p. 90°. This pure material had an activity of 2.32, 2.36 (ave., 2.34) μc./mmole.

Separation of Solids.—Residue A was mixed with 50 ml. of petroleum hexane, poured onto a column (4 × 100 cm.) containing 800 g. of chromatographic grade alumina (Merck and Co.), and eluted with hexane. Naphthalene passed through first, then benzothiophene. The naphthalene was purified by two crystallizations from alcohol, then sublimation at 60° (750 mm.); yield 46 mg., m.p. and mixed m.p. sharply at 80°. Its activity was determined to be 1.31, 1.39 (ave., 1.35) μc./mmole.

To purify the crude benzothiophene sufficiently for radioactive assay it was mixed with 2.5 ml. of water, 10 ml. of glacial acetic acid and 2.5 ml. of 30% hydrogen peroxide. After warming the mixture for 30 min. at 100°, 35 ml. of water was added and the mixture was left at 5° for several hours. The precipitated benzothiophene 1,1-dioxide was dried at 80°, then was heated for an hour at 75° (0.5 mm.) in a sublimation apparatus. No naphthalene appeared. The dioxide was thrice recrystallized from benzene-methylcyclohexane (1:2) to yield 52 mg. of pure product, m.p. and mixed m.p. 142°. Its activity was 0.93, 0.87 (ave., 0.90) μc./mmole.

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

Pyrolytic Formation of Arenes. III. Pyrolysis of Pyridine, Picolines and Methylpyrazine

BY CHARLES D. HURD AND JUSTINE I. SIMON[1]

RECEIVED MARCH 12, 1962

Products from the pyrolysis at 825–850° of pure picoline-free pyridine included quinoline, benzonitrile, acetonitrile, acrylonitrile and benzene. The picolines were much less stable than pyridine, products being pyridine, isomeric picolines, quinoline, nitriles, benzene, some ethylene but no acetylene. Analytical methods were developed for these mixtures. Methylpyrazine is considerably less stable to heat than any of the picolines. More acetonitrile and acrylonitrile were formed than from the picolines, and benzene was not found.

Since benzene, naphthalene, 3-methylthiophene and other pyrolytic products were obtained from 2-methylthiophene,[2,3] it was of interest to test carefully purified 2-picoline, 3-picoline, 4-picoline and pyridine itself under comparable thermal conditions.

Earlier pyrolytic work with pyridine and its homologs is not large. Roth,[4] the first to study pyridine by passing it through a red hot glass tube, noted hydrogen cyanide and bipyridines as products. Meyer and Hofmann-Meyer[5] reported 2,2′-bipyridine as the chief product, but they also found the 2,3′- and 2,4′-isomers.

Ruhemann[6] used temperatures of 600 to 900°. At the lower temperatures (600–650°) he reported that production of hydrogen and bipyridine was the chief reaction, whereas with increasing temperatures nuclear scission into hydrogen cyanide be-

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[1] University Fellow, 1953–1954; National Science Foundation Fellow, 1954–1955.

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

[3] C. D. Hurd, R. V. Levetan and A. R. Macon, *ibid.*, **84**, 4515 (1962).

[4] C. F. Roth, *Ber.*, **19**, 360 (1886).

[5] H. Meyer and A. Hoffmann-Meyer, *J. prakt. Chem.*, **102**, 287 (1921).

[6] S. Ruhemann, *Braunkohle*, **28**, 749 (1929); *Erdöl u. Teer*, **5**, 455 (1929). The two articles are identical.

TABLE I

PYROLYSIS OF PICOLINES

Temp., °C.	Contact time, sec.	Recovered subst., %	Products, mole %[a] a	b	c	d	e	f	g	h	i	j
						2-Picoline						
700	11	93	0.0	0.0	0.0	..	tr.	..	0.0	0.0	..	64
725	8	89	.0	.0	.0	..	8.4	..	0.0	.0	..	53
750	12	86	.0	.0	.0	..	9.2	..	1.5	.0	..	51
775	20	70	.13	.7	.2	0.0	21	..	4.9	.3	0.0	44
800	14	59	.26	.7	.5	0.4	21	..	2.4	.5	..	42
825	11	46	.39	1.3	.5	1.1	25	..	1.2	.7	.3	47
850	11	29	.57	1.3	.4	1.1	25	..	1.3	.35	.8	41
						3-Picoline						
700	18	85	0.0	0.0	0.0	..	3.3	tr.	..	..	..	61
750	20	66	.0	.0	.0	..	14	2.1	..	..	..	56
775	12	70	.0	.0	tr.	1.0	13	3.5	..	3.9	..	47
800	20	23	.19	.7	0.3	..	20	3.4	..	..	..	32
800	12	55	.10	.5	.2	1.3	16	4.2	..	3.0	.7	50
825	18	21	.25	1.0	.5	..	24	3.2	..	..	..	48
850	13	19	.48	1.3	.4	1.5	21	2.6	..	1.2	.9	34
						4-Picoline						
700	9	94	0.0	0.0	0.0	..	3.7	0.0	0.0	..	..	16
750	13	83	.0	.0	.0	..	8.0	.3	1.0	..	..	30
775	15	69	.0	tr.	tr.	..	14	.4	2.0	..	..	58
800	12	63	.31	0.6	0.6	..	20	.7	2.2	..	..	41
825	20	27	.40	1.2	.4	0.6	20	.9	1.4	..	.3	41
850	24	6	.48	0.8	.2	..	7.4	.3	0.5	..	..	26

[a] a, benzene; b, acetonitrile; c, acrylonitrile; d, benzonitrile; e, pyridine; f, 2-picoline; g, 3-picoline; h, 4-picoline; i, quinoline; j, residue in wt. %.

came important. At 900°, he stated that practically complete cleavage of the ring occurred, forming gaseous cleavage products. In addition to HCN he reported this gas analysis for the temperature range 700–900°: H_2 84–86%, CH_4 12–14%, olefins 1–2%, with no more than a trace of acetylene.

Krumholz[7] passed 6 kg. of commercial pyridine, b.p. 113.2–114.5°, through a quartz tube at 850° during three days. The products, with yields based on unrecovered pyridine, were 2,2′-bipyridine 10%, the 2,3′-isomer 10%, the 3,4′-isomer 4% and quinoline 2%. Also isolated were other bipyridines, terpyridyls, indole and indolizine. Some evidence was indicated also for pyrrole, 2-picolinonitrile, benzonitrile and dihydroskatole. Since there was no assurance that his pyridine was free of picolines which may have been responsible for the quinoline, it became a matter of importance to study pure pyridine from this point of view.

There is still less reported work on the picolines and most of this is on 2-picoline. Meyer and Hofmann-Meyer[5] exposed the latter to "red heat" and believed that 6,6′-dimethyl-2,2′-bipyridine was in the oily product boiling between 210–295°, but this conclusion was challenged by Wibaut[8] who prepared the latter and reported that it had different properties from the pyrolytic material. Meyer's product may have contained 2,2′-ethylenedipyridine $(NC_5H_4CH_2-)_2$, later synthesized[9] and found it to melt at 50°. This low melting point explains why it might have failed to crystallize from the oil found by Meyer and Hofmann-Meyer.

Just as toluene breaks initially into the benzyl radical, so also the picolines break initially[10] at 800° and 2 to 15 mm. pressure into the picolyl radicals. Bond energies for 2-, 3- and 4-picoline of 75.5, 76.5 and 77.5 kcal./mole, respectively, proved to be remarkably close to toluene's (77.5). Gaseous products were hydrogen and methane in a 3:2 ratio from 2- or 3-picoline, and 7:3 from 4-picoline. That pyridine was formed (21% yield) from 2-picoline at 800° was reported by Ameniya and Suzaki.[11]

Pyridine was purified for the present work to remove traces of picoline. This material yielded quinoline and benzonitrile on pyrolysis at 825–850°, thus confirming Krumholz's report.[10] Also found were other nitriles and benzene. That benzene was found is remarkable. In an experiment at 825° and 9 seconds contact time, one-third of the pyridine was recovered and from the remainder these yields were formed: benzene 0.18 mole %, acetonitrile 0.2, acrylonitrile 0.4, benzonitrile 1.1, quinoline 1.3, and a considerable higher boiling residue. Yields of the nitriles were about doubled at 850° (5 sec.) and were much less at 800° (12 sec.).

The several picolines were pyrolyzed at temperatures between 700–850°. Table I summarizes the data. Gaseous products and some carbonaceous

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(7) P. Krumholz, *Selecta chim.*, **8**, 3 (1949).

(8) H. Willink, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **54**, 275 (1935).

(9) P. G. Campbell and P. C. Teague, *J. Am. Chem. Soc.*, **76**, 1371 (1954).

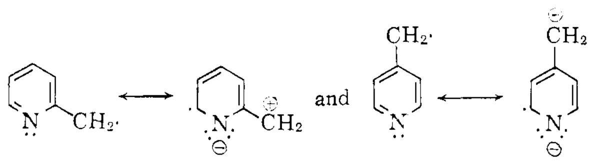
(10) J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **16**, 981 (1948).

(11) T. Ameniya and M. Suzaki, Japan Patent 4578 (1952); *C. A.*, **47**, 11260 (1953).

deposit appeared in all of the runs. The gas, chiefly hydrogen and methane, was analyzed for unsaturated hydrocarbons in several of the runs. Acetylene was absent, but about 1 mole % of ethylene, based on unrecovered picolines, appeared in the runs at 800° and about 2 mole % at 850°. Hydrogen cyanide was formed in every run above 775°, but no attempt was made to estimate it quantitatively.

In the experiment with pyridine at 825° (9 sec.) 64% was recovered, and at 850° (5 sec.) 57% was recovered. The much smaller recoveries of the picolines at these temperatures, with even shorter periods of heating, demonstrate that they are much less stable than pyridine. Decomposition rates of the three picolines vary but little among themselves between 700 to 775°. This would be expected in view of Szwarc's finding that bond dissociation energies of the three picolyl radicals were so nearly identical. From 800 to 850° some differences were observed: 2-picoline was the most stable isomer and 4-picoline the least. It is above 775° that benzene and nitriles first appeared, indicative of rupture of the ring.

The slightly larger bond dissociation energy reported by Szwarc for 4-picoline (77.5 kcal.) over 2-picoline (75.5) is not incompatible with the greater instability of 4-picoline found in the present study. Szwarc was dealing with the formation of the picolyl radicals as the slower, rate-determining step and suggested that the small differences might follow if dipole radicals were present in the resonance hybrid



The 2-picolyl dipole radical, with the least separation of charge, would be expected to be the most easily formed and the most stable, hence most resistant to further decomposition.

The appearance of some pyridine at the relatively low temperature of 700° is what one would expect if the primary, rate-determining reaction is formation of the picolyl radicals, followed by fast secondary reactions: $C_5H_4NCH_3 \rightarrow C_5H_4NCH_2\cdot + H\cdot$, and $C_5H_4NCH_3 + H\cdot \rightarrow$ either $C_5H_4NCH_2\cdot + H_2$, or $C_5H_5N + CH_3\cdot$. That pyridine production should decrease above 850° would be expected since pyridine itself decomposes fairly rapidly at this temperature.

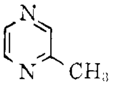
Rearrangement from one picoline to another was noticed at 725 and 750°, but there was no production of benzene or nitriles until higher temperatures were used. The fact that pyridine formation occurs at a somewhat lower temperature than picoline isomerization suggests a higher activation energy for the latter process than the former.

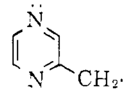
The low boiling products were of particular importance for several reasons. Except for the small size of the fractions (below 90°) they were relatively easy to isolate and characterize. Even so, they had been completely neglected by earlier investigators. Benzene had never been suspected. Benzene and the nitriles obviously were formed as the result of ring breakdown. Benzene production from all three picolines increased with increasing temperatures up to 850°, with somewhat larger yields coming from 2-picoline. A smaller yield of benzene was observed from pyridine than from any picoline.

The pyrolysis of 2-methylthiophene[3] gave rise to much hydrogen sulfide, pointing to rupture of both carbon–sulfur bonds. Comparable rupture of all carbon–nitrogen bonds in picoline would have yielded ammonia, but no ammonia was noticed. That one of the nuclear C–N bonds breaks on heating, however, is evident because of nitrile formation. Creation of the cyanide group evidently is a large driving force in this reaction. Since all carbon–nitrogen bonds were not broken this speaks also against the transient existence of $:CH—CH{=}CH—CH{=}\underset{\cdot}{C}—CH_2\cdot$ (followed by hydrogen shift to $:CH—CH{=}CH—CH{=}CH—CH:$ and cyclization to benzene), comparable to the formation[2] of cyclopentadiene *via* $\cdot CH{=}CH—CH{=}\underset{\cdot}{C}—CH_2\cdot$ from the 2-thienyl radical. Although such a postulate would have explained benzene from picoline, it would not have explained benzene from pyridine.

Also, the data speak against any formation of benzene *via* acetylene since no acetylene was formed. Nor could there have been any significant production of benzene *via* gaseous olefins. The highest quantity of such olefins ever found was 2.2 mole % and in this run (3-picoline at 850°) the amount of simple arenes isolated (benzene, benzonitrile, quinoline) totaled nearly 4 mole %. The unidentified arenes in the large tarry residue would increase this to a much larger figure. When one considers that 2 to 3 moles of propylene or ethylene would be consumed in forming each new benzene ring the whole process becomes quite unreasonable.

No prior work has been reported on the pyrolysis of methylpyrazine (I), but it should be capable of pyrolytic change into the pyrazinylmethyl radical II if it follows the pattern set by toluene, methylthiophene and picoline. Conceivably, II might break on heating into the C_3H_3 fragment[2] from which benzene would be a predictable product. Offsetting this, however, is the fact that nitrile


I


II

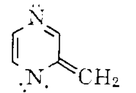

III

TABLE II

METHYLPYRAZINE

Temp., °C.	800	825
Contact time, sec.	10	15
Subst. taken, g.	10.5	7.6
Subst. recovd.,[a] %	25	(5)
Products,[b] mole %		
Benzene	0.0	0.0
Acetonitrile	15	22
Acrylonitrile	2	10
High boiling residue, wt. %	37	53

[a] Contained some pyrazine, as judged by new peaks in the infrared spectrum. [b] Gases (H_2, hydrocarbons, HCN) and some carbonaceous matter also were formed.

TABLE III

INFRARED ABSORPTION BANDS FOR THE PICOLINES

Weak bands			Medium bands			Strong bands		
2-	3-	4-picoline	2-	3-	4-picoline	2-	3-	4-picoline
2.09	2.09	2.09	..	..	..	..	..	..
2.23	2.23	2.28	..	..	..	..	..	..
2.40	2.40	2.40	..	..	..	..	..	..
..	..	2.68	..	..	..	..	..	..
2.89	2.90	2.90	..	..	..	..	..	..
..	..	..	..	..	..	3.30	3.30	3.30
3.66	3.66	3.65	..	..	..	..	..	..
3.81	3.83	3.83	..	..	..	..	..	..
..	4.06	4.13	..	..	4.06	..	..	..
..	4.22	4.30	..	..	..	..	..	..
4.49	..	4.42	..	..	..	..	..	..
..	..	4.52	..	..	..	..	..	..
..	4.92	4.91	5.01	..	..	..	..	..
..	5.09	..	5.10	..	5.14	..	..	..
..	..	..	5.21	5.21	..	..	..	..
..	5.35	5.39	5.32	..	..	..	..	..
5.43	5.45	..	..	..	..	..	..	..
5.85	..	5.70	..	5.81	..	..	..	..
			..	6.01	5.99	..	..	..
			..	..	..	6.2–6.4	6.25	6.21
			..	..	..	..	6.33	6.35
			..	..	..	..	..	6.65
			..	..	..	6.72–7.01	6.75–7.10	6.9–7.1
			..	..	..	7.26	7.22	7.21
..	..	..	..	7.50	..	..	..	..
..	..	7.72	..	..	..	7.72	..	..
			..	8.00	..	8.08	8.12	8.13
			8.31	..	..	..	..	8.21
..	..	..	..	..	..	..	8.40	..
..	..	8.92	..	..	..	8.70	8.85	..
			..	..	9.10	9.06	9.03	..
			..	..	..	..	..	9.29
			..	..	..	9.52	9.59	9.57
			..	..	..	..	9.70	..
			..	10.15	..	10.01	..	10.00
			..	..	..	10.26	..	10.26
			10.6sh[a]	..	10.5sh	..	..	..
..	..	..	..	10.86	..	..	..	..
..	..	..	11.28	..	11.41	..	..	..
11.96	..	..	..	..	..	..	..	..
			12.35sh	..	..	12.50sh	12.5–12.8	12.4–12.5
			..	..	..	13.0–13.4	..	..
			..	..	..	13.68	..	13.69
..	..	..	..	..	13.9sh	..	14.0	..
..	..	15.0	..	..	..	..	..	..

[a] sh = shoulder.

formation was important in the decomposition of the picolines and that the carbon-to-nitrogen bond of the ring cleaved only on one side. This tendency for nitrile production should be even more pronounced with methylpyrazine in view of the two nitrogen atoms in the ring. This, indeed, is what was found to occur. No benzene was in the products but acetonitrile and acrylonitrile were formed in much greater yields (Table II) than from the picolines. Methylpyrazine also was found to be much less stable than the picolines.

Acetonitrile is readily visualized as a cleavage product of I or II and acrylonitrile as a cleavage product of III. Both II and III are members of the same resonance hybrid.

Experimental

Pyridine.—A mixture of 135 ml. of pyridine, 2.5 l. of water and 90 g. of potassium permanganate was stirred at 100° for 2 hours. It was filtered from manganese oxides 15 hours later and solid sodium hydroxide (about 500 g.) was added to the filtrate until pyridine separated as a top layer. This layer was separated, dried for 12 hours over solid potassium hydroxide, then was refluxed with calcium oxide for 3 hours. It was distilled (114.5°) through a Davis column.[12] The infrared spectrum of this pure pyridine showed these peaks: weak at 2.40, 2.90, 3.87, 4.09, 4.30, 4.45, 4.65, 5.45, 5.70, 7.72, 10.60, 11.28, 12.30; medium at 5.00, 5.18, 5.32, 5.91, 6.10, 7.25, 7.35; strong at 3.30, 6.2–6.3, 6.75, 6.94, 8.18, 8.65, 9.32, 9.65, 10.10, 13.4, 14.0 μ. The methiodide[13] melted at 117–119°.

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[12] H. Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

[13] A. Hantzsch, *Ber.*, **42**, 81 (1909), listed the m.p. at 116°.

Picolines.—Commercial samples of the three picolines were taken. Each, in turn, was converted into its sulfate (0.2 mole of picoline, 100 ml. of water, 0.2 mole of concd. sulfuric acid) and steam was passed through the solution to remove any hydrocarbons, after which the bases were recovered by dropwise addition of concd. sodium hydroxide solution with efficient cooling. The layer of picoline was decanted, dried over sodium hydroxide pellets, refluxed with calcium oxide for 2 to 4 days, and finally distilled through the Davis column. These boiling points were obtained: 2-picoline, 128.3–128.5°; 3-picoline, 143.5°; 4-picoline, 143.0°. Infrared spectra are given for the pure compounds in Table III. These methiodides were prepared: 2-picoline methiodide, m.p. 230.5–231.5°, literature[14] 230°; 3-picoline methiodide, m.p. 93.5°, literature[14] 92°; 4-picoline methiodide, m.p. 151°, literature[15] 152°.

Method.—The compounds were pyrolyzed essentially as described by Hurd and Levetan.[3] The hot reaction tube delivered into a 50-ml. ice-cooled flask connected by tubes in series to another 50-ml. flask cooled to −78°, a drying tube containing NaOH pellets, a bubbler containing 0.1 *N* sulfuric acid, a 3-way stopcock before delivering uncondensed gas into a 4-l. bottle to collect the brine displaced by the gas. For gas analysis, the 3-way stopcock was turned to take the analytical sample directly, but never until at least 500 cc. of gas had been first collected thus ensuring removal of all nitrogen from the train.

Analytical samples were taken and analyzed for ethylene and acetylene in a modified Orsat apparatus. Potassium iodomercurate[16] solution was used in the search for acetylene and 8% fuming sulfuric acid for ethylene.

Identification of Liquid Products.—The more volatile fractions of the condensate were separated by distillation through the Davis column. Hydrogen cyanide was recognized by odor and identified by m.p. (−14°) and b.p. (26°). It sharp infrared band at 5.78 μ revealed it as a component in some of the other low boiling fractions.

Benzene was characterized as *m*-dinitrobenzene.[3] Acetonitrile was found not to interfere. Infrared absorption at 5.42 μ also was used. Acetonitrile was identified by its infrared band at 10.85 μ and by conversion into two solid derivatives, namely, *p*-bromophenacyl acetate, m.p. 83–84°, and α-iminoethylmercaptoacetic acid hydrochloride, m.p. 114–115°. Nitrile samples of 5 drops were sufficient. To make the former, the nitrile was hydrolyzed to acetic acid by refluxing 2 hours with sulfuric acid (20 drops of concd. acid to 5 drops of water), diluting with 30 drops of water, fractionating to separate all that distilled at 95–100°, neutralizing the distillate to *p*H 6 with sodium hydroxide solution, then adding 60 drops of ethanol and 0.1 g. of *p*-bromophenacyl bromide followed by and refluxing for 2 hours. On cooling, the crystalline derivative was collected and recrystallized from alcohol.

To make the second derivative, a mixture of 5 drops of nitrile, 5 drops of mercaptoacetic acid and 2 ml. of dry ether was saturated with hydrogen chloride gas and left for 24 hours at 5–10°. The crystals were separated and rinsed with absolute ether.

Acrylonitrile was recognized by its rapid decolorizing action on bromine in carbon tetrachloride. It was identified by infrared spectral comparison of the fractions obtained in pyrolysis and known mixtures containing acrylonitrile. The most prominent peak is near 10.4 μ.

Analysis of Volatile Products.—The infrared method was selected, using 5.42 μ for benzene, 10.85 μ for acetonitrile and 11.42 μ for acrylonitrile. Curves for the analysis of mixtures of these compounds were prepared by obtaining log I_0/I values[17] from known mixtures using data of Table IV.

Identification of the Pyridine Bases.—These compounds were detected and analyzed by infrared spectra, taking known synthetic mixtures as standards. Table V lists data for specific absorption bands in various mixtures. Graphs were drawn, plotting log I_0/I values against percentage composition. The pyridine peaks at 5.18, 8.18, 8.65 μ, respectively, were used in its mixtures with 2-, 3- and 4-picolines. The mixture being analyzed was placed in the "sample cell" of a Baird double beam recording infrared spectrophotometer. In some of the readings, a rock salt crystal was placed in the "solvent well," and for others a pure picoline was put in the "solvent cell." A micro-cell was used as the "sample cell" in many of the determinations, making it possible to do a run with 2 or 3 drops of sample.

TABLE IV

INFRARED ANALYSIS OF KNOWN MIXTURES

Known % by wt.	Benzene	Acetonitrile	Acrylonitrile
1	11.0	78.9	10.1
2	21.4	38.8	39.8
3	42.3	18.9	38.8
4	72.0	9.1	18.9
log I_0/I at	5.42 μ	10.85 μ	11.42 μ
1	0.098	0.908	0.042
2	.162	.414	.174
3	.326	.193	.164
4	.604	.105	.067

TABLE V

ANALYSIS OF MIXTURES OF PYRIDINE BASES

Mixt. of A, B	% A by wt.	log I_0/I	Microns	Subst. in solvent cell or well
Pyridine, 2-picoline	10.3	0.026	5.18	2-Picoline
	20.5	.050		
	50.8	.123		
Pyridine, 3-picoline	5.1	0.70	8.18	3-Picoline[a]
	10.2	.136		
	20.3	.262		
Pyridine, 4-picoline	5.1	.068	8.65	Rock salt[b]
	10.2	.126		
	20.4	.250		
2-Picoline, pyridine	1.0	.084	7.72	Rock salt
2-Picoline, B-1[c]	4.8	.157		
2-Picoline, B-2[d]	9.9	.316		
2-Picoline, B-3[e]	5.0	.124		
2-Picoline, B-4[f]	2.0	.048		
3-Picoline, 2-picoline	5.0	.139	8.40[g]	2-Picoline
	10.1	.276		
	20.2	.537		
3-Picoline, 4-picoline	1.0	.120	14.0[h]	Rock salt
	5.0	.610		
	10.0	1.061		
3-Picoline, 4-picoline	5.0	0.098	8.40[i]	Rock salt
	10.0	.189		
	20.0	.348		
4-Picoline, 3-picoline	5.0	.171	10.0	Rock salt
	10.0	.338		
	20.0	.670		

[a] 2-Picoline did not interfere. [b] 2-Picoline interferes if present in more than a few per cent. [c] Pyridine 85, 3-picoline 5, 4-picoline 5. [d] Pyridine 10, 3-picoline 40, 4-picoline 40. [e] Pyridine 5, 3-picoline 88, 4-picoline 2. [f] Pyridine 2, 3-picoline 91, 4-picoline 5. If the 3-picoline content exceeds 50% as in *e* and *f* a separate calibration curve must be drawn (compare *c*, *d*). The intercepts of these curves depart slightly from zero since pyridine and 4-picoline each have a tiny band at 7.72 μ. [g] Very minute amounts of 3-picoline in 2-picoline may be detected by the broad bands in the 12.6 and 14 μ regions. [h] Accurate if the 3-picoline concentration is less than 5%. [i] Used with 3-picoline concentrations above 5%.

Analyses for pyridine, 2- and 3-picolines were quite satisfactory, but analysis for 4-picoline was troublesome. When 4-picoline was present in 2-picoline it was always accompanied by 3-picoline and it was impossible to estimate it

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(14) F. Wild, "Characterisation of Organic Compounds," Cambridge University Press, England, 1947, p. 245.

(15) E. A. Coulson and J. I. Jones, *J. Soc. Chem. Ind.*, **65**, 169 (1946).

(16) C. D. Hurd and L. U. Spence, *J. Am. Chem. Soc.*, **58**, 3353 (1929).

(17) N. Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

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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[18] R. G. Jones, E. C. Kornfeld and K. C. McLaughlin, *Ind. Eng. Chem. Anal. Ed.*, **72**, 3539 (1950).

[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).