μc./mmole. To change such a figure to the observed 1.35 μc. calls for dilution with naphthalene containing either zero or 1.28 μc./mmole. Thus far we have thought of no plausible mechanism to account for such naphthalene in sufficiently large quantities. A small amount could be expected in these steps: $C_4H_3SC^*H_3 \rightarrow C_4H_4S \rightarrow$ both Ib and II. Then 2 Ib $\rightarrow C_6H_6$, and diene addition of this benzene to II would yield naphthalene of zero activity.

Details of procedure will be elaborated in the papers which follow.

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

Pyrolytic Formation of Arenes. II. Benzene and Other Arenes from Thiophene, 2-Methylthiophene and 2-(Methyl-^{14}C)-thiophene

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Thiophene is more stable thermally than 2-methylthiophene. The gaseous products from both exclusive of hydrogen sulfide, from experiments at 800–825°, consisted only of hydrogen and methane. No acetylene or ethylene was detected. Benzene was definitely established as a pyrolytic product of thiophene at 825°, affording evidence for thermal weakness of nuclear bonds. That the C–H bonds of thiophene are weak also, yielding bithiophenes, has long been known. Under thermal conditions yielding benzene, naphthalene, anthracene and related products from toluene, 2-methylthiophene pyrolyzes into thiophene, benzene, hydrogen sulfide, cyclopentadiene, carbon disulfide, naphthalene, benzothiophene, 2,2′-vinylenedithiophene and 3-methylthiophene. A method of separating benzene as such as developed for small volumes of mixtures which are rich in thiophene and low in thiophene that consists in converting the thiophene component into methyl 2-thienyl ketone and then volatilizing the benzene. Synthesis of 2-(methyl-^{14}C)-thiophene from $^{14}CO_2$ is described, from steps involving thenoic-α-^{14}C acid, 2-thenyl-α-^{14}C alcohol, 2-thenyl-α-^{14}C chloride as intermediates. Radioactive benzene, naphthalene and benzothiophene were isolated as pyrolytic products at 800°, having activities that were 182, 105 and 70% as great, respectively, as the starting methylthiophene.

In the preceding paper[2] reasons were presented for thinking that 2-methylthiophene might produce benzene as a pyrolytic product. Before undertaking this study we investigated toluene so as to establish conditions for the pyrolysis. Using a flow method at 825° and atmospheric pressure, with contact times of 4 to 7 seconds, we obtained conditions that yielded essentially the products described by Berthelot[3] and Ferko.[4] Benzene was found in yields up to 22%. From the less volatile products were isolated naphthalene (m.p. 76–78°, mixed m.p. 78–81°) and a solid of m.p. 200–210° which was presumed to be anthracene. At the time this work was performed naphthalene was one of the expected products. That it was indeed found becomes significant in view of the fact that Errede and Cassidy[5] made no mention of it as a product from toluene at 970°, 0.002 sec. contact time, and 0.5 mm. of pressure.

The conditions that we found for toluene were then used with 2-methylthiophene. Two samples of the latter were studied. One, supplied by The Texas Company, was made by dehydrogenation of pentane[6] with sulfur dioxide over alumina–chromia. Infrared analysis of this material pointed to the presence of both 3-methylthiophene (from isopentane in the pentane) and 1–2% of toluene. 3-Methylthiophene would not interfere in the interpretation since any benzene arising from it would come by the same path as that proposed from 2-methylthiophene. The amount of toluene was not considered large enough to vitiate results since the maximum conversion of pure toluene into benzene at 825° was about 20%, suggesting that the benzene arising from the toluene in the methylthiophene would be no more than 0.2–0.4%.

The second sample of 2-methylthiophene was synthesized from sodium levulinate by heating it with P_4S_7. It contained no toluene or 3-methylthiophene. The pyrolytic products obtained from both samples of 2-methylthiophene were quite comparable.

Benzene was a product. Other products were cyclopentadiene, carbon disulfide, hydrogen sulfide and thiophene. They were characterized by chemical tests as well as by infrared spectra.

Considerable attention was paid to the characterization of benzene in the benzene–thiophene fraction. It was realized that more thiophene than benzene would be present; hence it was necessary to develop an analysis of thiophene–benzene mixtures containing only 5–25% of benzene. Such mixtures differ enormously from the thiophene–benzene mixture which has been studied so much in the past, namely, technical benzene which contains 99.5–99.9% of benzene.

Three methods of analysis were developed. One was infrared analysis, scrutinizing peaks at 5.1, 5.5 or 6.77 μ which are typical for benzene but not shown by thiophene. The optical density was found to vary linearly with benzene content in the thiophene at 5.1 and 5.5μ. A second method was combustion analysis of the mixture for carbon, since benzene is 92% C and thiophene is 57% C. This relationship also is linear. Deviation of known mixtures by either method was within ±1%. In the pyrolytic runs some cyclopentadiene (91% C) was present; hence the combustion

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(1) (a) The Texas Co. Fellow, 1954–1955; (b) U. S. Rubber Co. Foundation Fellow, 1958–1959.

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

(3) M. Berthelot, *Ann. chim. phys.*, [4] **9**, 453, 471 (1866); **12**, 143 (1867); **16**, 144 (1869); *Bull. soc. chim.*, [2] **22**, 437 (1874).

(4) P. Ferko, *Ber.*, **20**, 660 (1887).

(5) L. Errede and J. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960).

(6) R. E. Conary, L. W. Devaney, L. E. Ruidisch, R. F. McCleary and K. L. Kreuz, *Ind. Eng. Chem.*, **42**, 467 (1950).

TABLE I

2-METHYLTHIOPHENE

Substance		Temp., °C.	Duration, min.	Contact time, sec.	Products, mole %[b]				
Source[a]	Recovd., %				C_6H_6	C_4H_4S	C_5H_{10}	H_2S	CS_2
T	91	725	36	6.1	0.15	2	0.4	2.2	0
S	87	725	42	7.1	.24	3.5	.5	1.8	0
T	66	775	33	5.3	1.3	11	.3	6.5	tr.
S	68	775	33	5.3	1.5	15	.3	2.9	tr.
T	9.4	825	52	8.0	3.9	23	.1	29	0.6
S	23	825	48	7.4	3.0	24	.1	26	0.6

[a] T = The Texas Co.; S = synthetic. [b] Based on unrecovered methylthiophene.

method would show "benzene plus cyclopentadiene." Any carbon disulfide would be present in too small an amount to interfere materially.

The third method was separation of the benzene as such. To this end, the thiophene of the mixture (80–90% thiophene) was converted into its methyl ketone by reaction with acetic anhydride and stannic chloride. This reaction is practically quantitative for thiophene but is without effect on benzene. The benzene was then separated readily from the higher boiling ketone (b.p. 213°) by distillation and changed into *m*-dinitrobenzene for confirmation.

Experiments were performed not only at 825° but at 775 and 725°. Results are summarized in Table I. Benzene was present among the products at all three temperatures, but the quantity was largest at the highest temperature. This supports the hypothesis that the 2-thenyl radical from 2-methylthiophene breaks into a C_3H_3 fragment as the precursor of benzene.

From the less volatile products of the reaction were separated benzothiophene and 2,2′-vinylenedithiophene.

Thiophene.—After studying 2-methylthiophene we studied thiophene since it was an important pyrolytic product of 2-methylthiophene. It was of particular interest to see if benzene also could arise from thiophene and if so under what conditions as compared with 2-methylthiophene. Less severe conditions would imply that the benzene arising from methylthiophene came *via* thiophene instead of C_3H_3 fragmentation.[2] More severe conditions would support the hypothesis that methylthiophene cleaves directly into a C_3H_3 radical.

Benzene was indeed found as a product from thiophene but thiophene was unquestionably more stable than 2-methylthiophene. In Table II it is seen that practically complete destruction of the latter took place at 800° as judged by the negligible amount of substance collected between 85–112°. Benzene was formed to the extent of about 1 mole per cent. In contrast, thiophene was decomposed only slightly at 800° as witnessed by the large fraction of product boiling to 84°, chiefly 82–84°, but there was extensive decomposition at 825°. To detect benzene in the distillate, reliance was put on a small peak at 6.71μ in the infrared spectrum. This peak was shown by a synthetic mixture of 1% benzene and 99% pure thiophene. The spectrum of the product from the 825°-experiment, boiling at 79–85°, also showed this absorption at 6.71μ but only with about half the intensity of the synthetic mixture. This suggested that the concentration of benzene in this fraction was about 0.5%. This small amount was undetectable by vapor phase chromatography with the column employed.

TABLE II

COMPARATIVE RUNS ON THIOPHENE AND 2-METHYLTHIOPHENE

	2-Methylthiophene		Thiophene	
Run	1	2	3	4
Subst. taken, ml.	21.0	21.5	50	25
Temp., °C.	800	800	800	825
Contact time, sec.	40	22	9	14
Liq. condensed at 0°, ml.	9	10	49	7.4
Liq. redistilled, g.				
To 84°	1.4	3.8	41.6	4.9
85–112°	0.2	0.0	...	...
Vol. of gas, less H_2S, l.	3.6	4.0	...	...
Composition, %				
Hydrogen	19	22	...	65
Methane	81	78	...	35
Yield, mole %				
Hydrogen	13	17	...	...
Methane	56	60		

Benzene as a pyrolytic product supports the statement made in the first paper of this series[2] that a significant thermal weakness exists in thiophene at a C–S bond as well as at C–H bonds. It seems established, however, that the bulk of benzene obtained from 2-methylthiophene did not come by way of thiophene.

Radioactive 2-Methylthiophene.—To prepare 2-(methyl-^{14}C)-thiophene, previously unsynthesized, these synthetic steps were selected:

$$SC_4H_3Br \rightarrow SC_4H_3MgBr \xrightarrow{^{14}CO_2} SC_4H_3\text{–}C^*OOH \xrightarrow{LiAlH_4}$$

$$SC_4H_3\text{–}C^*H_2OH \xrightarrow{SOCl_2} SC_4H_3\text{–}C^*H_2Cl \xrightarrow[AcOH]{Zn} SC_4H_3\text{–}C^*H_3$$

Although the only new procedure in these operations was reduction of 2-thenoic acid with lithium aluminum hydride, each step had to be developed for maximum yield in view of the small quantities involved.

2-Thenyl alcohol is unstable to acid; hence the customary decomposition of the lithium and aluminum salts (following the $LiAlH_4$ redution) was found to be unsuitable. Use of saturated ammonium chloride solution proved to be satisfactory.

It was our original intention to subject the thenyl alcohol to hydrogenolysis, but this reduction was not achieved at 3 atm. hydrogen pressure using either palladium-on-charcoal or copper chromite catalysts. The alcohol, therefore, was converted to the chloride which, in turn, was reduced.

In the final distillation step of the 2-(methyl-^{14}C)-thiophene the product was first diluted with ordinary 2-methylthiophene obtained from The Texas Co. Although the latter contained small amounts of toluene and 3-methylthiophene it was known (see above) that they did not contribute significantly to the formation of benzene. Starting with 5 millicuries of radioactive barium carbonate we obtained 54.5 g. (0.56 mole) of 2-(methyl-^{14}C)-thiophene having an activity of 1.28 μc./mmole, or an over-all yield of 14.3% based on the recovered radioactivity.

Unsuccessful efforts were made to oxidize the methyl group to carboxyl using alkaline potassium permanganate. Thus we were unable by direct experiment to demonstrate that all of the activity was in the side chain; but in view of the method of synthesis, and of the experience (see paper IV) with toluene-α-^{14}C, it may safely be assumed that such was the case.

Pyrolysis of the radioactive 2-methylthiophene also was carried out at 800° but for a somewhat shorter contact time than was used for the non-radioactive substance. These products were separated and assayed for their radioactivity in μc./mmole: benzene (as *m*-dinitrobenzene) 2.34, naphthalene 1.35, benzothiophene (as its 1,1-dioxide) 0.90. The activity of the benzene is 182% that of the original methylthiophene, that of naphthalene 105%, and that of benzothiophene 70%. Conversion of benzene into *m*-dinitrobenzene was necessary for purification, since the infrared spectrum of the isolated benzene showed a number of foreign peaks. The interpretation of these data was presented[2] in paper I.

Experimental

Apparatus.—A vertical electric furnace was used, the temperature being controlled automatically at its hottest point to ±2°. The effective hot zone was 29 cm. The reactor tube was of fused silica, 62 × 1.95 cm. (inside diam.) and it carried a Pyrex thermocouple well. The thermocouple was placed in approximately the middle of the furnace in the hottest zone. Thus, the fore part of the furnace served as preheater. As an example, for a 6-cm. hot zone at 775°, the temperature tapered off to 725° about 7 cm. above it and 8 cm. below it. This 21-cm. length, representing about 60 cc., was arbitrarily used as the basis for the calculation of contact times.

The measured sample was placed in a side-arm test-tube connected to a vaporizer, which was another side-arm test-tube heated at 210–230° by a salt-bath. The arm of the vaporizer, insulated against heat loss, delivered into the top of the unpacked quartz reactor tube. The sample entered the reaction tube (previously flushed with nitrogen) at a uniform rate by mercury displacement.[7] Products were condensed from the effluent vapors in two traps, one cooled by ice and salt and the other by Dry Ice and acetone. Uncondensed gas was discarded.

Reagents.—Toluene was scrubbed (concd. H_2SO_4) and distilled within a 1° range; $n^{20}\mathrm{D}$ 1.4969. Its infrared spectrum showed no strong absorption between 14.8–15.0 μ where benzene absorbs strongly. Virtual absence of 2-methylthiophene was shown by no absorption[8] at 11.8 or 12.2 μ.

Thiophene, obtained from Matheson, Coleman and Bell, was dried over potassium hydroxide and distilled, b.p. 83.5–84°. Vapor phase chromatography revealed only a single peak. Its infrared spectrum showed it to be free of benzene and toluene by comparison with spectra published by the American Petroleum Institute.

2-Methylthiophene.—(a) From The Texas Company: b.p. 110–111°, $n^{20}\mathrm{D}$ 1.5198. Its infrared spectrum showed a large band at 13.07 μ attributable to 3-methylthiophene. It also showed large absorption at 13.68 μ and several smaller peaks at 6.21, 6.68, 9.28, 9.68 μ which were absent in pure 2-methylthiophene. The last five bands came from toluene. The infrared spectrum of a mixture of pure 2-methylthiophene (below) containing 2% of toluene showed similar peaks at these five points.

(b) **Synthetic Material.**—This 2-methylthiophene was made in 43% yield (pure) from sodium levulinate (100 g.), P_4S_7 (250 g.) and sand (50 g.) following established procedures[9]: b.p. 110–111°,[10] $n^{20}\mathrm{D}$ 1.5203.[11] The infrared spectrum was identical to that published by Hartough.[8]

Pyrolysis of Toluene at 825°.—The combined condensed products (14.5 g.) from 21.8 g. (25 cc.) of toluene were collected from a period lasting 33 minutes, or a contact time of 5.7 seconds. This material was redistilled through a Davis column.[10] There was collected 4.0 g. of benzene at 78–90°, 1.4 g. of toluene ($n^{20}\mathrm{D}$ 1.4976) and 5.2 g. of higher boiling residue. The benzene was confirmed as its *m*-dinitro derivative. Some naphthalene, m.p. 76–78°, was obtained on processing the residue. Its mixed m.p. with authentic naphthalene was 78–81°.

Pyrolysis of 2-Methylthiophene.—Temperature was the major variable in the several runs. The quantity taken was 25.5 g. (25 ml.) and the contact time in the hot zone was 5 to 8 sec. No more than a trace of decomposition was noticed at 675°, 6.2 sec., but products were formed at 725–825°. The results that were reported in Table I represent minimum values since losses undoubtedly occurred during manipulations.

Infrared Characterizations.—These peaks were significant for the components in the reaction mixture (w = weak, s = strong): cyclopentadiene: 3.47w, 6.15, 7.32s, 8.10w, 10.4, 10.9, 11.1s, 12.4 μ; benzene: 2.40w, 3.29, 5.09w, 5.50w, 6.77, 9.62, 15.2μ; carbon disulfide: 4.31w, 4.60, 6.60μ; thiophene: 5.52, 5.68w, 7.12, 7.81w, 9.24, 11.5w, 12.0μ; 3-methylthiophene: 6.46, 10.1, 10.65, 11.8, 12.2 broad, 13.1μ; 2-methylthiophene: 3.24, 3.42, 3.50, 5.60, 6.51, 6.95, 8.07, 8.60, 9.26, 9.58, 11.8, 12.2, 14.1–14.8μ; toluene: 3.28, 3.40, 3.48, 5.12, 5.40, 5.53, 6.20, 6.66, 6.82, 7.24, 8.46, 9.23, 9.68, 11.16, 12.7, 13.6–13.9, 14.4μ.

A Baird double beam recording spectrophotometer was employed with rock salt cells. Many spectra were obtained without solvent; hence no solvent cell was used for them but instead there was used a single piece of sodium chloride of thickness comparable to the windows of the sample cell. Spectra of some of the mixtures were obtained by using a solvent cell of suitable thickness and containing one of the components in pure state to simplify the spectrum obtained. Comparison of the spectra of known mixtures with those of the fractions of the unknown reaction products made it possible to verify qualitatively and estimate semi-quantitatively the compounds in question. Each component also was checked chemically.

Qualitative Characterization of the Products.—Cyclopentadiene was identified as its adduct with maleic anhydride. The maximum quantity of diene obtained was 50 mg., but this was ample. To make the adduct the fraction was mixed with 0.1 g. of maleic anhydride dissolved in 0.5 cc. of benzene. After standing for 2 hours at 25° the mixture was evaporated and the resultant solid was crystallized from ligroin; m.p. 158–162 and mixture m.p. 160–162°.

The hydrogen sulfide in the effluent gas was determined by titration with standard iodine solution.

Carbon disulfide was detected in trace amounts by heating the suspected sample with alcoholic potassium hydroxide, adding a solution of cupric chloride and acidifying. Bright yellow copper xanthate separated.[12] The test is distinctive and not shown by hydrogen sulfide or thiophene. Thiophene was characterized by b.p. (80–84°) and by a positive indophenin test.

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[7] C. D. Hurd and F. D. Pilgrim, *J. Am. Chem. Soc.*, **55**, 757 (1933).

[8] H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., 1952, New York, N. Y.

[9] W. Kues and C. Paal, *Ber.*, **19**, 555 (1886); W. Steinkopf, "Die Chemie des Thiophens," Th. Steinkopff, Dresden, 1941, p. 34.

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

[11] F. S. Fawcett, *J. Am. Chem. Soc.*, **68**, 1420 (1946), also reports this figure.

[12] J. V. Dubsky, *J. prakt. Chem.*, **93**, 142 (1916).

Analysis of Thiophene–Benzene Mixtures by Infrared Methods.—Absorption bands at 5.1 and 5.5μ were taken. For the band at 5.1μ, these values for log I_0/I were obtained for solutions of benzene in thiophene which contained 5, 10, 20% of benzene, respectively: 0.041, 0.086, 0.166. For the band at 5.5μ, the comparable values were 0.060, 0.124, 0.251. The plots from these values are linear.

Separation of Benzene from Thiophene.—This method was developed for mixtures containing 10–20% of benzene and for volumes of 0.5–1.0 cc. Into a flask fitted to a reflux condenser, which was protected with a drying tube, was placed 1 cc. (or less) of the benzene–thiophene mixture and 2 cc. of acetic anhydride. The flask was cooled for several minutes by an ice–salt-bath, then 1.2 cc. of fresh stannic chloride was added dropwise through the condenser. The purple mixture was warmed to 20° and finally was heated on a steam-bath for 15–20 minutes. After cooling, 2 cc. of glacial acetic acid was added through the condenser to rinse any benzene into the flask.

The contents of the flask were distilled to 114° and the distillate was caught directly in a receiver resembling a narrow-necked Babcock milk test bottle of about 10-cc. capacity. Aqueous salt solution was then added to precipitate the benzene and bring it up into the neck.

To make a derivative, the small benzene layer was nitrated with 1.5–2 cc. of concd. sulfuric acid, followed by an equal volume of concd. nitric acid. Unremoved thiophene was noticed by darkening at this stage, but the color rapidly changed to light yellow if the separation was adequate. The mixture was heated for 15 minutes on a steam-bath, then was poured over 15–20 g. of ice. Pale yellow, flocculent *m*-dinitrobenzene precipitated. It was crystallized from methanol–water; m.p. 86–88°, mixture m.p. 87.5–88.5°.

One-cc. samples of the thiophene–benzene fractions of both of the 825°-runs were separated in this manner, giving rise to 0.08 g. of dinitrobenzene from one run (T) and 0.05 g. from the other (S).

Higher Boiling Products.—The high-boiling residues from four 25-g. runs at 775–825° were collected (31 g.). A preliminary separation by distillation at 0.02 mm. yielded (A) 5.6 g. at 74–94°, (B) 0.12 g. at 100–110° and (C) 6.1 g. at 110–160°. Redistillation of A gave 1.03 g. of a fraction at 35–65° (0.02 mm.) made up of a white solid and a blue liquid. The solid was naphthalene, m.p. 61–70° without further recrystallization. Its picrate melted at 148–149.5° after one crystallization from ethanol; mixture m.p. with a known sample of m.p. 151–153° was 148.5–151.5°. It will be shown later that benzothiophene also is in this fraction.

Fractions B and C were processed by Miss Justine Simon. From C was collected a fraction (about 2 g.) at 85–110° (0.02 mm.) that changed to a yellow solid, the major part of which was 2,2′-vinylenedithiophene,[13] m.p. 132–133.5° after two crystallizations from methanol. Its analysis was acceptable (Calcd.: C, 62.46; H, 4.20. Found: C, 62.17; H, 4.37) and it gave a positive indophenin test. Fraction B also was essentially this compound. Lower melting products came from the filtrate, but no purification technique (distillation, crystallization, chromatography) sufficed to purify them to an identifiable state.

Comparative Pyrolyses of Thiophene and 2-Methylthiophene.—A Vycor reaction tube was used in these runs instead of the fused silica tube; otherwise the operative details were essentially those described above. The Vycor tube was 25 mm. in diameter. The hot volume was 65 cc. Liquid products were condensed in two traps, one at 0° then another at −78°. Uncondensed gas was passed through a bubbler containing sodium hydroxide solution (to absorb H_2S) and then was collected by displacement of saturated salt solution. Results are summarized in Table III.

2-Methylthiophene.—In runs 1 and 2, the gas was shown to contain only hydrogen and methane. Acetylene and ethylene were absent. Gas phase chromatography at room temperature was the method used for analysis, the absorbent being 3,3′-oxydipropionitrile on firebrick in a 45-ft. column. With nitrogen as carrier and by injecting known samples, it was found that hydrogen could be detected but that hydrocarbons (CH_4, C_2H_4) could not. With helium as carrier all the hydrocarbons from methane up could be detected, but hydrogen could not. As a matter of fact, known mixtures of propane and propylene could be separated satisfactorily in this way and the propylene detected even if its amount was less than 0.5%. In runs 1 and 2, with helium as carrier, only methane was detected, whereas with nitrogen as carrier gas only hydrogen was detected.

Table III

Analysis of Volatile Liquid Products from 2-Methylthiophene

Component	Known mixture, % Taken	Known mixture, % Found	Fraction A Found	Fraction B Found
Carbon disulfide	12.8	15.0	8	0
Benzene	15.0	17.4	19	9
Thiophene	68.6	66.0	72	55
2-Methylthiophene	3.6	1.6	1	36

For quantitative work, equal volumes of methane and of gas from the runs were injected, in turn, into the column and their retention volumes compared. Thus, the gas from runs 1 and 2 were 81, 78% methane, respectively. Since only methane and hydrogen had been found, the quantity of hydrogen was 19, 22%, respectively, by difference.

Redistillation of the 1.6 g. of distilled product from run 1 yielded 0.33 g. up to 58°, 0.24 g. at 58–78°, 0.79 g. at 78–84° (fraction A) and 0.58 g. at 31° and 90 mm. (fraction B). The last two fractions were analyzed by vapor phase chromatography at 59.5° in a 6-ft. column packed with tritolyl phosphate. The components were determined by comparing their retention times with known compounds determined at the same time. The amount of each component was calculated by comparing its retention volume with the total retention volume. Results are listed in Table III. In addition to the prominent peak for 2-methylthiophene in fraction B there was a very small peak just beyond it. This may have been caused by 3-methylthiophene, but no known sample was available as a check.

A black viscous tar from run 2, remaining after distillation of the volatile portion, weighed 7.3 g. A fraction containing naphthalene and benzothiophene was separated from it by vacuum distillation. This was treated with acetic acid and hydrogen peroxide. Naphthalene, undissolved, was separated by filtration and characterized by m.p., mixture m.p. and infrared spectrum. In the filtrate was benzothiophene 1,1-dioxide which was separated and similarly characterized. Yields of 0.4 mole % each were observed.

Thiophene.—In run 3 (Table II) only a trace of carbonaceous deposit was on the walls of the reaction tube. The 41.6 g. of liquid product collected up to 84° had an infrared spectrum between 2–8 μ that was indistinguishable from that of pure thiophene. There was no absorption at 6.7 μ, showing absence of benzene.

In run 4, decomposition was much more extensive as evidenced by the considerably smaller amount of liquid product and the formation of such a large quantity of carbonaceous deposit as to nearly clog the tube. The infrared spectrum of the 4.9-g. fraction revealed a small peak at 6.71 μ. Comparison with spectra of known thiophene–benzene mixtures led to the conclusion that the distillate contained 0.5% of benzene. It is noteworthy that this concentration of benzene was not detectable by vapor phase chromatography. The black, oily residue of run 4, after removal of volatile material, weighed 1.5 g.

The gaseous products were collected and found to consist of 35% methane and 65% hydrogen by gas phase chromatography. Ethylene, acetylene or other hydrocarbons were not detected. The volume of the gas was not measured.

Radioactive 2-Methylthiophene. 2-Thenoic-α-^{14}C Acid.—A Grignard reagent was made from 1.2 g. of magnesium turnings, 8.2 g. of 2-bromothiophene and 60 ml. of dry ether. Fifty ml. of this solution, containing 38.5 mmoles of Grignard reagent by titration, was carbonated with $^{14}CO_2$ in a manner similar to that described in paper IV for phenylmagnesium bromide except for two changes. The reaction flask was cooled to the temperature of liquid nitrogen instead of −78°. This permitted the reagent to be frozen solid and allowed the system to be evacuated to 0.1 mm. pressure. The other modification was dilution of the 5 millicuries of radioactive barium carbonate (80 mg.) with anhydrous sodium carbonate (3.3900 g.) instead of with ordinary barium carbonate. The 0.4 mmole of $Ba^{14}CO_3$ plus the 32.4 mmoles of Na_2CO_3 gave 32.8 mmoles of available car-

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[13] W. Steinkopf and H. Jacob, *Ann.*, **501**, 188 (1933), list 132.5° for this compound; H. Keskin, C. Mason and F. F. Nord, *J. Org. Chem.*, **16**, 1333 (1951), list 130.5–131°.

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

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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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