(b) **Atropic Acid.**[6]—Tropic acid (280 mg.) was refluxed with a solution of potassium hydroxide (0.8 g.) in water (2 ml.) in a nitrogen atmosphere for 40 min. The cooled solution was acidified with dilute hydrochloric acid; crude atropic acid (181 mg., 72%), m.p. 102.5–107.5°, separated. Recrystallization from aqueous methanol afforded colorless prismatic needles, m.p. 105–107.5°.

(c) **Cleavage of the Atropic Acid.**—Atropic acid (143 mg.) was dissolved in a solution of sodium carbonate (51 mg.) in water (5 ml.) and cooled to 0°. Osmium tetroxide (10 mg.) was added, the solution becoming pale brown and then purple. A solution of sodium metaperiodate (449 mg.) in water (10 ml.) was then added slowly to the stirred solution during 45 min. Stirring was continued for 24 hr. maintaining the temperature at 0°. The reaction mixture which was then pale yellow was extracted with ether to remove osmium tetroxide and then acidified with 2 N hydrochloric acid. Ether extraction of this solution yielded crude phenylglyoxylic acid which was converted to its oxime (84 mg., 53%), m.p. 141.5–144°, by the method of Ahmad and Spenser.[7] The oxime was sublimed prior to radioactive assay. The aqueous solution from which the phenylglyoxylic acid had been extracted was distilled and the aqueous distillate added to a solution of dimedone (280 mg.) in water (100 ml.). After standing overnight, colorless needles of the formaldehyde-dimedone derivative (153 mg., 55%), m.p. 192–193°, separated. It was crystallized from aqueous ethanol prior to assay.

(d) **Decarboxylation of Phenylglyoxylic Acid Oxime.**—The oxime (47 mg.) was suspended in water (18 ml.) which had been previously boiled to remove carbon dioxide. The mixture was then refluxed in a current of pure nitrogen which was subsequently passed through a solution of barium hydroxide to collect the evolved carbon dioxide. The yield of barium carbonate was 27 mg. (48%). Extraction of the residual aqueous solution with ether yielded benzonitrile which was hydrolyzed by heating with glycerol (0.6 ml.) and potassium hydroxide (0.4 g.) at 200° for 1 hr. Acidification of the reaction mixture with hydrochloric acid and extraction with ether yielded benzoic acid which was sublimed and crystallized from water; 3 mg., 9%, m.p. 121–122°, not depressed on admixture with an authentic specimen.

Benzoic acid was also obtained by the direct oxidation of the tropic acid with potassium permanganate.[3] The benzoic acid was decarboxylated by heating with sodium azide and concentrated sulfuric acid using established procedures.[16] The resultant aniline was isolated as its benzoyl derivative.

The activities of the degradation products of the alkaloids are recorded in Table I, calculated for undiluted material.

---

[16] S. Shibata, I. Imaseki and M. Yamazaki, *Pharm. Bull. (Japan)* **5**, 594 (1957).

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

Pyrolytic Formation of Arenes. I. Survey of General Principles and Findings

BY CHARLES D. HURD, A. R. MACON, JUSTINE I. SIMON AND R. V. LEVETAN

RECEIVED MARCH 12, 1962

A survey is made of the pyrolytic formation of arenes from hydrocarbons and of various hypotheses designed to explain the findings. It is pointed out that C_3-fragments are important, hitherto unrecognized intermediates in the production of benzene and other arenes. In particular, there is the propadienyl–propargyl resonance hybrid (Ia) that is considered to arise from propylene, toluene, methylthiophene or picoline and the isomeric trimethine fragment Ib, ·CH=CH—CH:, both a radical and a carbene, that is formed from Ia by a 1,2-hydrogen shift or from hetero-arenes (as thiophene or pyridine) by direct rupture of the nucleus. It is shown how Ib may account for benzene by dimerization and for naphthalene, benzothiophene or quinoline by addition to benzyl, 2-thenyl or picolyl radicals, respectively. A resonance-stabilized C_4H_4 diradical II, ·CH=CH—CH=CH·, is considered to be formed along with Ia by thermal scission of benzyl, and it arises also from thiophene or pyridine by rupture of the nucleus. The role of II in giving rise to naphthalene from toluene, benzothiophene from thiophene, or quinoline from pyridine is outlined. The 2-thenyl radical not only ruptures into Ia but it also rearranges into 3-thenyl. A transition state involving a 3-membered ring is postulated to account for this 1,2-shift. Similarly, all of the picolyl radicals shift reversibly into their isomers, and undoubtedly the α-carbon of the benzyl radical wanders at high temperature to different nuclear carbons in parallel fashion. Experiments on which these conclusions are based are discussed. They deal with the pyrolysis of derivatives of thiophene and pyridine, and with labeled (^{14}C) toluene and 2-methylthiophene.

Work of long standing has demonstrated that the formation of arenes by pyrolysis may start with other arenes or with aliphatic substances. It will be shown in this and the following papers that arenes may be formed also from heterocyclic substances. To arrive at a common basis of understanding for these seemingly unrelated pyrolytic syntheses it is helpful to examine the pertinent past work.

Arenes from Aliphatics.—Of the several hypotheses that have been suggested starting with alkenes (or alkanes), these figure prominently.

a. **Acetylene Hypothesis of Berthelot.**—Berthelot[1] proposed that a hydrocarbon may pyrolyze into a denser hydrocarbon, ultimately into acetylene which may then polymerize in part into benzene or styrene, that the acetylene may continue to react yielding naphthalene or anthracene, and that for any particular high temperature there exists a complex equilibrium. Although this hypothesis has been shown to be unrealistic (see below), it has influenced thinking up to fairly recent times. Thus, in pyrolyzing pyridine at 900° Ruhemann[2] reported that no more than a trace of acetylene, if any appeared in the gaseous products. He added: "während Azetylenkondensationsprodukte aromatischer Natur überhaupt nicht auftreten." Thus, Ruhemann noted the absence of acetylene and arenes but he obviously accepted Berthelot's acetylene hypothesis as the basis of arene formation.

b. **CH_2 and CH Radicals.**—The suggestion that CH_2 and CH fragments serve as precursors of arenes was put forward by Bone and Coward.[3]

c. **Butadiene or Conjugated Dienes as Precursors of Thermal Aromatization.**—This concept was based on Staudinger's observation[4] that butadiene yielded a tar at 800° of which 30.6% was benzene and 25% was naphthalene. D. T. Jones[5]

---

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

[2] S. Ruhemann, *Braunkohle*, **28**, 749 (1929).

[3] W. Bone and H. Coward, *J. Chem. Soc.*, **93**, 1201 (1908).

[4] H. Staudinger, R. Endle and J. Herold, *Ber.*, **46**, 2466 (1913).

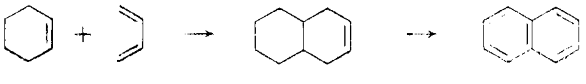
and others followed this lead, stressing the idea that conjugate unsaturation rather than acetylene was the necessary precursor of arenes. He supported this viewpoint by citing the non-production of acetylene at any stage of formation of coal tar.

d. A Diene Synthesis for Arenes.—Davidson's hypothesis[6] that benzene was formed by thermal addition of ethylene to butadiene antedates Diels and Alder's first publication of the diene synthesis by more than a decade. Oddly, however, Davidson's proposal never has been mentioned in the several surveys[7] of the diene synthesis that have appeared.

Davidson heated an ethane–propane mixture at several temperatures between 550–900°, finding much aromatization, some butadiene, but no acetylene unless some was added in advance. If even as little as 0.1% acetylene was added, then a positive test was found for it after the heating. This evidence speaks powerfully against Berthelot's acetylene hypothesis. To explain aromatization, Davidson postulated "union of the ethylene and butadiene to form cyclohexane which most likely has no separate existence, breaking down at once into benzene and hydrogen." Davidson probably meant cyclohexene instead of cyclohexane, in view of his accompanying equation

$$\begin{array}{l} \text{cyclohexane} \xrightarrow{-H_2} \text{cyclohexane} \longrightarrow \text{butadiene} + \text{ethylene} \\ \qquad\qquad\qquad\qquad\qquad\qquad \hookrightarrow \text{benzene} + \text{hydrogen} \end{array}$$

Wheeler and Wood[8] extended this idea. From olefins (C_2H_4, C_3H_6, C_4H_8) at 500–700° they found cyclohexene as well as benzene. They extended the hypothesis to include naphthalene formation



The only prior explanation of the pyrolytic formation of naphthalene was Berthelot's *via* styrene and acetylene.

e. Cyclic trimerization of alkenes, followed by dehydrogenation or dealkanation, was suggested[9] during pyrolytic studies of such olefins as propylene and isobutylene. The products reported were benzene, toluene, naphthalene, phenanthrene, anthracene and other arenes. Isobutylene yielded much propylene but no butadiene.

Although cyclohexanes or cyclohexenes were not unreasonable intermediates *via* (d) or (e) there is a major objection, namely, that cyclohexane (or cyclohexene) pyrolyzes chiefly into butadiene[10a] with no evidence for arenes unless a catalyst is present; furthermore, butadiene is synthetically prepared[10b] from cyclohexene by pyrolysis.

f. Formation of Arenes by Way of C_3-Fragments.—This approach has not been generally recognized in spite of evidence accumulating in its favor. For example, more propylene was formed than any other hydrocarbon following the heating of ethylene[11] at 575° for 4 minutes. Also, the large production of arenes from propylene, cited above,[9] is noteworthy. It has been established[12] also in work with biallyl, 4-methyl-1-butene, allylcyclohexane or 4-phenyl-1-butene that an allylic C–C bond is relatively weak toward pyrolytic scission. Pyrolysis of terpene hydrocarbons[13] displays the same weakness toward thermal rupture at allylic positions.

In the pyrolysis of propylene, Szwarc[14] demonstrated that allene was a product (686–872°, low pressures), postulating formation of an allyl radical in the first step

$$CH_2{=}CHCH_3 \xrightarrow{-H} CH_2{=}CHCH_2\cdot \xrightarrow{-H} CH_2{=}C{=}CH_2$$

We now propose that thermal abstraction of a hydrogen atom from allene yields the propadienyl radical: $CH_2{=}C{=}CH_2 \rightarrow \cdot CH{=}C{=}CH_2 + H\cdot$. Propadienyl and propargyl are equivalent since these radicals constitute the propadienyl-propargyl resonance hybrid: $\cdot CH{=}C{=}CH_2 \leftrightarrow CH{\equiv}C{-}CH_2\cdot$ (Ia). At the high temperatures involved a 1,2-shift of hydrogen should occur readily, yielding the trimethine[15] fragment Ib, $\cdot CH{=}CH{-}CH{:}$, which is both a radical and a carbene. It, too, is stabilized by resonance, $\cdot CH{=}CH{-}CH{:} \leftrightarrow {:}CH{-}CH{=}CH\cdot$.

Dimerization of Ib should give rise to benzene: $2C_3H_3 \rightarrow C_6H_6$. This hypothesis is presented to explain the large production of arenes on heating propylene.

Arenes from Aromatics.—Aromatic hydrocarbons as pyrolytic source materials for other arenes fall into two groups: those without and those with side chains. Benzene, with no side chain, is much more stable thermally than toluene, and its mode of decomposition is dramatically different. It changes into biphenyl, terphenyl, 4,4′-diphenylbiphenyl, whereas toluene yields no bi-*p*-tolyl. Instead, it pyrolyzes into benzene, 1,2-diphenylethane and polycyclic hydrocarbons (naphthalene, anthracene, phenanthrene, etc.).

Berthelot,[1] Ferko,[16] and others studied toluene in the early years, but the more recent significant studies have been by Szwarc, Steacie and Errede. Szwarc,[17] using low pressure, short duration of heating and a temperature of 845°, obtained only benzene and 1,2-diphenylethane in the liquid

---

(5) D. T. Jones, *J. Chem. Soc.*, **107**, 1582 (1915); *J. Soc. Chem. Ind.*, **36**, 3 (1917); C. Weizmann, E. Bergmann, *et al.*, *Ind. Eng. Chem.*, **43**, 2312, 2318 (1951).

(6) J. G. Davidson, *ibid.*, **10**, 901 (1918).

(7) J. Norton, *Chem. Revs.*, **31**, 319 (1942); K. Alder, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 381–507; H. Holmes in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 60–173.

(8) R. V. Wheeler and W. Wood, *J. Chem. Soc.*, 1819 (1930).

(9) C. D. Hurd and L. U. Spence, *J. Am. Chem. Soc.*, **51**, 3561 (1929); C. D. Hurd and R. N. Meinert, *ibid.*, **52**, 4978 (1930); C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934).

(10) R. N. Pease and J. Morton, *J. Am. Chem. Soc.*, **55**, 3190 (1933); G. S. Whitby and M. Katz, *Ind. Eng. Chem.*, **25**, 1338 (1933). (b) E. B. Hershberg and J. Ruhoff, *Org. Syntheses*, **17**, 25 (1937).

(11) F. Frey and D. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); H. Groll, *ibid.*, **25**, 784 (1933).

(12) C. D. Hurd and H. T. Bollman, *J. Am. Chem. Soc.*, **55**, 699 (1933).

(13) H. Pines and J. Ryer, *ibid.*, **77**, 4370 (1955); H. Pines and R. H. Kozlowski, *ibid.*, **78**, 3776 (1956); H. Pines and C. Chen, *ibid.*, **81**, 928 (1959).

(14) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

(15) I.U.P.A.C. rule A-4.1 lists methylidyne as the name of $CH{\equiv}$ and permits methine as the name of $={C}-$; *J. Am. Chem. Soc.*, **82**, 5550 (1960). The alternative name of Ib according to Rule A-4.4 is 1-propen-1-yl-3-ylidene.

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

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

products. The gas was methane (2/5) and hydrogen (3/5). The initial, rate-determining step was scission into benzyl and hydrogen

$$PhCH_3 \longrightarrow PhCH_2\cdot + H\cdot$$

following which it was assumed that hydrogen attacked toluene bidirectionally

$$\begin{array}{l} PhCH_3 + H\cdot \longrightarrow PhCH_2\cdot + H_2 \\ \quad\searrow \\ \qquad PhH + CH_3\cdot \xrightarrow{PhCH_3} PhCH_2\cdot + CH_4 \end{array}$$

The termination step of this chain reaction was union of two benzyl radicals to form 1,2-diphenylethane. Steacie[18] supported this mechanism, testing it with toluene-α-d_3, $PhCD_3$.

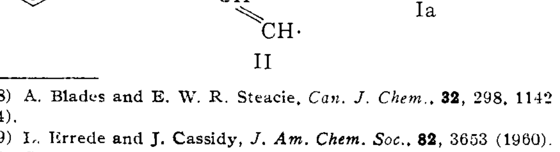
Errede and Cassidy[19] studied toluene at 0.5 mm. pressure, 0.002 sec. contact time and 970°. They found 1,2-diphenylethane, diarylmethanes, anthracene, a trace of stilbene, but no naphthalene or phenanthrene. Similar pyrolysis of 1,2-diphenylethane gave rise to diphenylmethane, *o*-benzyltoluene, anthracene and *trans*-stilbene. The yield of anthracene was low (2–16%) from either toluene or 1,2-diphenylethane, but it was high (91–95%) from *o*-benzyltoluene or 9,10-dihydroanthracene. The fact that no naphthalene or phenanthrene was found suggests that the stated temperature of 970° may have been considerably above the effective temperature, which is probable in view of the very short contact time.

Errede stated that the initially-formed benzyl radicals combined reversibly into 1,2-diphenylethane: $2PhCH_2\cdot \rightleftarrows PhCH_2CH_2Ph$, but that "eventually recombination occurs irreversibly (perhaps on the reactor wall) affording *o*-methylated diarylmethane. This in turn can undergo dehydrogenation to yield anthracene as stable end product."

The Problem.—The present investigation concerns itself with the mechanism of pyrolysis of toluene and the pyrolytic synthesis of benzene and other arenes. It will be seen that of necessity the investigation also includes heterocyclic compounds.

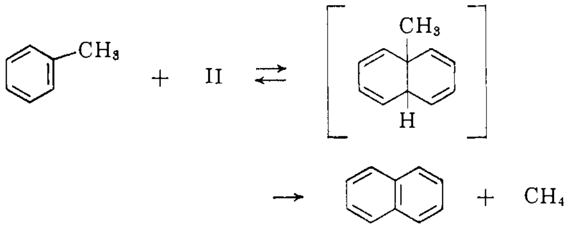
That toluene breaks initially into benzyl has been established beyond question, but how this radical changes into benzene, naphthalene, anthracene, phenanthrene, etc., is less evident. Errede's hypothesis seems reasonable as one pathway leading to anthracene, but it does not explain formation of the other products.

Pyrolytic C_3- and C_4-Fragmentation by Way of Reverse Diene Synthesis.—Eleven years ago, one of us proposed[20] an explanation for the formation of arenes from toluene as a working hypothesis. Essentially, the proposal involved fragmentation of the benzyl radical in the manner of a reverse diene synthesis into C_4- and C_3- radicals



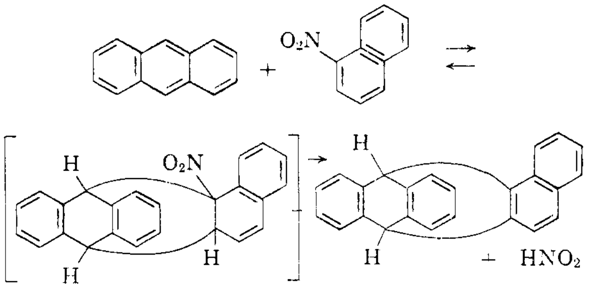
Fragment II is stabilized by resonance and one member of the resonance hybrid, :CH—CH=CH—CH:, reveals double bond character at the central carbons, stabilizing this diradical against scission into two molecules of acetylene. Fragment Ia, also stabilized by resonance, is the propadienyl–propargyl moiety described above as arising from propylene or allene. Its facile isomerization into trimethine (Ib) by 1,2-shift of hydrogens and dimerization into benzene would, therefore, be the same as outlined above for the production of benzene from propylene: 2Ia → 2Ib → C_6H_6. The benzene that is formed in this way would supplement that produced[17,18] by attack of hydrogen radical on toluene: $C_6H_5CH_3 + H\cdot \rightarrow C_6H_6 + CH_3$.

Fragment II provides one explanation for the naphthalene which arises from toluene. The steps would be reversible addition of II to toluene followed by irreversible loss of methane. Comparable



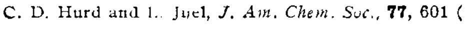
addition of II to toluene at the 2,3- or 3,4-positions, followed by loss of hydrogen at the bridgehead, would yield 1- or 2-methylnaphthalene.

Such a diene synthesis of naphthalene is comparable to Wheeler and Wood's[8] proposal for naphthalene formation *via* cyclohexene and butadiene, but it differs in having a C_4-diradical as the "diene" rather than butadiene itself. Comparable also is the thermal synthesis[21] of 7,12-dihydro-7,12-*o*-benzenobenz[a]anthracene from 1-nitronaphthalene and anthracene at 300°



Two plans suggested themselves to test the above hypothesis that the toluene nucleus may undergo pyrolytic rupture, namely, the use of isotopically labeled toluene and the pyrolysis of heterocyclic analogs of toluene. The general findings will be summarized in this paper, but the details will be presented in papers II, III, IV which follow.

2-Methylthiophene.—Just as propylene initially yields the allyl radical, or toluene the benzyl radical, so it follows that 2-methylthiophene should cleave into the 2-thenyl radical,



---

[18] A. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298, 1142 (1954).

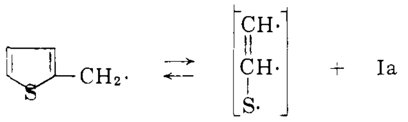
[19] L. Errede and J. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960).

[20] C. D. Hurd, papers of "Twelfth National Organic Chemistry Symposium of the Am. Chem. Soc.," Denver, Colo., June, 1951, p. 114.

[21] C. D. Hurd and L. Juel, *J. Am. Chem. Soc.*, **77**, 601 (1955).

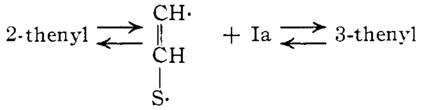
Its dimerization into 1,2-di-2-thenylethane would be analogous to the dimerization of benzyl into 1,2-diphenylethane, but no dithenylethane was found among the products from 2-methylthiophene. The related compound 2,2′-vinylenedithiophene (1,2-di-2-thenylethylene) was obtained, however, in the present work: $2\,SC_4H_3CH_2\cdot \rightleftarrows SC_4H_3CH_2\text{-}CH_2C_4H_3S \xrightarrow{-2H} SC_4H_3CH{=}CHC_4H_3S$, a reaction analogous to the formation of stilbene from toluene.

The 2-thenyl radical may break into Ia at the high temperature of the experiment, analogous to the rupture of benzyl into Ia

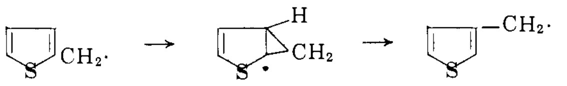


Dimerization of Ib (from Ia) should yield benzene. Thiophene would be anticipated also, by attack of the hydrogen atom on methylthiophene: $SC_4H_3{-}CH_3 + H\cdot \rightarrow C_4H_3S + CH_3\cdot$

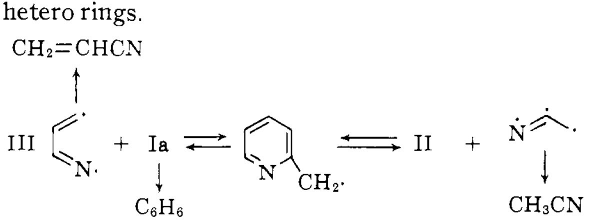
Benzene was indeed formed. The other products that were definitely identified were thiophene, cyclopentadiene, hydrogen sulfide, carbon disulfide, 3-methylthiophene, benzothiophene, naphthalene and 2,2′-vinylenedithiophene. Some of the 3-methylthiophene may have been formed by recombination of the fragments

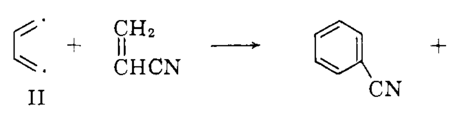

$$\text{2-thenyl} \rightleftarrows \begin{matrix} CH\cdot \\ \| \\ CH \\ | \\ S\cdot \end{matrix} + \text{Ia} \rightleftarrows \text{3-thenyl}$$

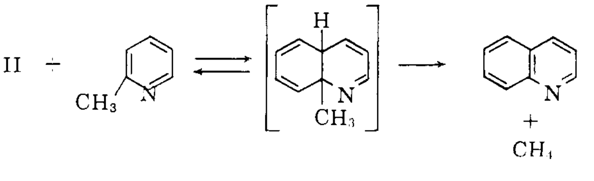
In view of the facile change of Ia into Ib that is believed to occur, this explanation probably would not account for much of the 3-thenyl radical that must have been formed. More likely, most of it came by rearrangement without fragmentation by way of a cyclic transition state



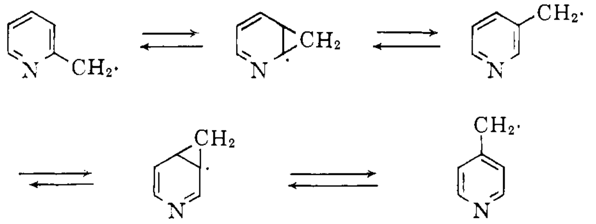
An explanation for the presence of cyclopentadiene, benzothiophene and naphthalene will be deferred to follow the material on the thermal rupture of hetero rings.



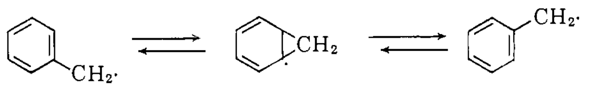




Picoline.—The three picolines were pyrolyzed similarly. As with the formation of benzyl from toluene or thenyl from methylthiophene it is logical to expect pyrolytic formation of the picolyl radical from picoline. Benzene would be expected from picolyl, *via* Ia and Ib, and indeed it was found as a product. Other products were acetonitrile, acrylonitrile, benzonitrile and quinoline. To explain them one may assume as shown in the formula diagram that the 2-picolyl radical breaks bidirectionally. Recombination of fragments Ia and III might yield either 2- or 3-picoline and both compounds were formed in the products; but so also was 4-picoline, and this is strong evidence for the intramolecular rearrangement involving neighboring positions in a cyclic transition state

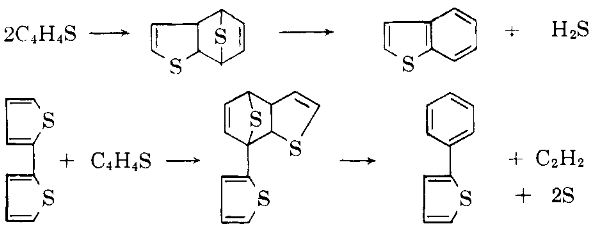


It is significant that one could detect rearrangements among the picolines at temperatures somewhat lower (725, 750°) than the minimum temperature (775°) observed for formation of benzene or nitriles. At higher temperatures (above 775°) the fragmentation route may have contributed. It follows that the benzyl radical formed from toluene "wanders" similarly



Such a mechanism would explain the formation of *o*- and *m*-xylene[22] during pyrolysis of *p*-xylene at 920° and about 0.2 sec.

Thermal Rupture of Unsubstituted Hetero Rings. Benzene from Thiophene or Pyridine.—The few pyrolytic studies on thiophene or pyridine that are on record have shown that the C–H bonds break, just as with benzene. Auwers and Bredt[23] reported formation of 2,2′- and 3,3′-bithiophene from thiophene at red heat. This was confirmed by Wynberg and Bantjes[24] at 800–850° who succeeded also in isolating 2,3′-bithiophene and a tar which contained much benzothiophene and possible traces of naphthalene, phenylthiophene and thiophthenes, based on mass spectral analysis. They explained the results by diene syntheses



Although the last equation shows acetylene as a product, it should be noted that no one actually

---

[22] J. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1955).

[23] K. v. Auwers and T. Bredt, *Ber.*, **27**, 1741 (1894).

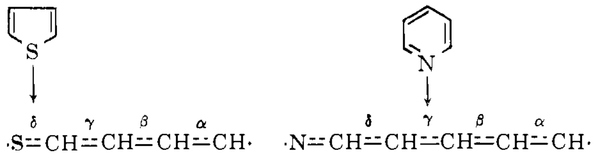
[24] H. Wynberg and A. Bantjes, *J. Org. Chem.*, **24**, 1421 (1959).

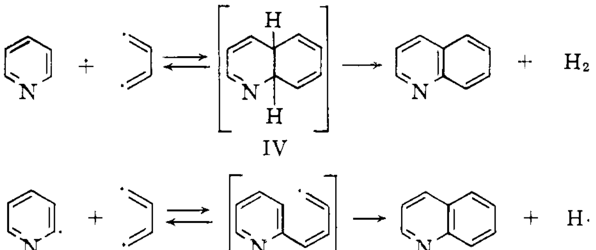
has found it from thiophene. Wynberg and Bantjes made no search for benzene as a reaction product.

That pyridine pyrolyzes to yield bipyridines was established by Roth[25] and confirmed by Meyer[26] who demonstrated that the major isomer was 2,2′-bipyridine with 2,3′- and 2,4′-bipyridines appearing in smaller amounts. Benzene was not mentioned.

In our work we established definitely that benzene is a pyrolytic product from both thiophene and pyridine, although somewhat higher temperatures were required than for their methyl homologs. Acetonitrile, acrylonitrile, benzonitrile and quinoline were formed also from pyridine.

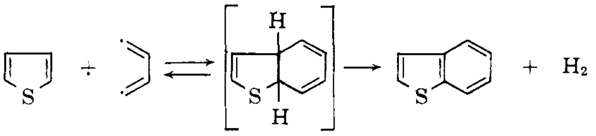
These findings point to significant thermal weakness at nuclear positions as well as at the carbon–hydrogen bonds. It may be assumed that the hetero bond (C–S or C–N) in thiophene or pyridine is the point of initial nuclear rupture into diradicals. After this occurs, somewhat random rupture of other bonds may be anticipated, but because of resonance stabilization the cleavage at positions marked γ or δ should be favored. Also, the virtual absence of acetylene in the products speaks against any extensive rupture at β. Rupture at γ would lead to Ib, above, which could dimerize to benzene. Rupture at δ would lead to II, above, and this is the radical that served to explain the formation of naphthalene from toluene, and quinoline or benzonitrile from picoline. It also explains the formation of quinoline from either pyridine or the pyridyl radical





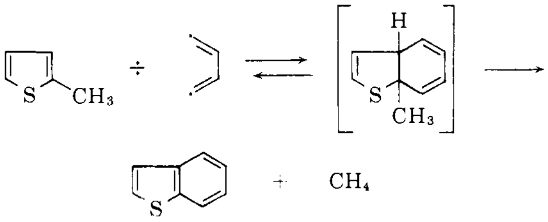
IV

Reaction of the C_4H_4 radical with thiophene would explain the benzothiophene that was observed by Wynberg and Bantjes. Although adduct V of this reaction might conceivably decompose into benzene, acetylene and sulfur, paralleling Wynberg and Bantjes' explanation of phenylthiophene, the plan has two objections: (1) acetylene was sought for but not found; (2) adduct IV of the comparable pyridine reaction would not be expected to break into C_6H_6, C_2H_2 and HCN nearly as readily as into quinoline plus hydrogen.

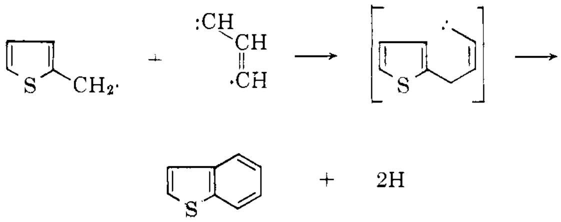


V

The benzothiophene which was observed from 2-methylthiophene could be explained analogously. Thiophene is formed in considerable quantity, and would cleave into II. Its union with methylthiophene would yield benzothiophene



Benzothiophene could arise also by addition of thenyl to Ib



The fact that cyclopentadiene was found in the products from 2-methylthiophene points to some nuclear C–S cleavage with the more prominent α-C–H cleavage. Such scission would yield $\cdot S\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}\underset{\cdot}{C}{-}CH_3$. Loss of sulfur and a 1,2-shift of hydrogen, which is reasonable at the high temperature, would give rise to $\cdot CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2\cdot$ (or the resonance hybrid, $\leftrightarrow :CH{-}CH{=}CH{-}CH{=}CH_2$) and this would cyclize to cyclopentadiene. Later, it will be shown that this C_5H_6 fragment may lead also to naphthalene.

Use of Tracer Methods.—Having demonstrated that the methyl homologs of thiophene and pyridine provided a powerful means of checking mechanistic considerations regarding the pyrolysis of toluene, we next turned to tracer methods using carbon-14 in the side chain of both toluene and 2-methylthiophene.

Toluene-$\alpha^{14}C$ obviously would give results uninfluenced by possible interferences from a hetero atom. Benzene formation could be pictured as (let C* = ^{14}C).

$$C_6H_5C^*H_3 \longrightarrow I^* + II;\ 2\,I^* \longrightarrow C_6^{**}H_6$$
$$C_6H_5C^*H_3 + H\cdot \longrightarrow C_6H_6 + C^*H_4$$

If benzene were formed exclusively by simple cleavage of the methyl group, none of it would be radioactive. The extent to which the carbon of the methyl group enters into the formation of benzene would then be determined by measuring the ^{14}C in the formed benzene. A very real amount was formed.

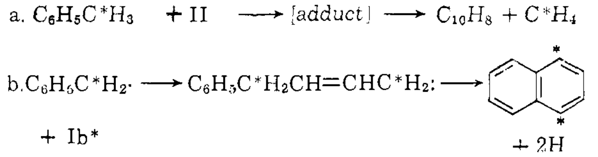
The activity of the toluene-$\alpha^{14}C$ was 1.32 μc. per millimole. The activity found for benzene was 0.043 μc. per mmole. These products were obtained also: naphthalene (0.232 μc./mmole), phenanthrene (2.26 μc./mmole) and anthracene (2.52 μc./mmole).

Two routes are suggested to explain the radioactivity of the naphthalene (a) and (b).

---

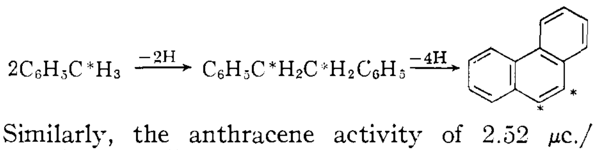
(25) C. F. Roth, *Ber.*, **19**, 360 (1886).

(26) H. Meyer and Alice Hofmann-Meyer, *J. prakt. Chem.*, **102**, 287 (1921).

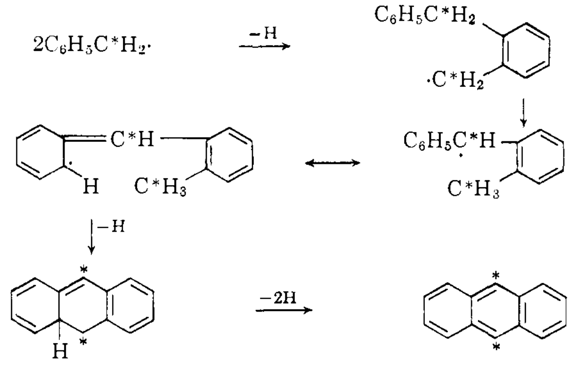


Plan a yields an inactive naphthalene, whereas plan b yields naphthalene with two ^{14}C atoms per molecule. Since the naphthalene found was only 17.6% as active as the toluene it follows that nine-tenths (91.2%) of it came by the diene mechanism a and the rest by b.

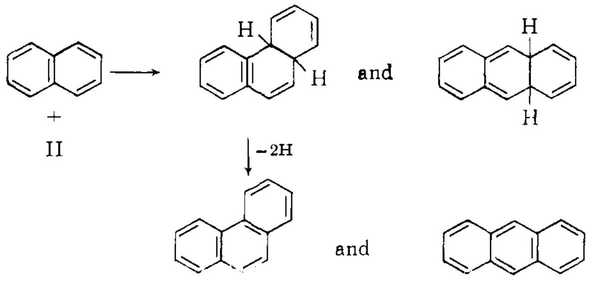
The phenanthrene activity of 2.26 μc./mmole indicates two ^{14}C atoms per molecule, supporting the generally accepted mechanism



Similarly, the anthracene activity of 2.52 μc./mmole, virtually twice that of the starting toluene, supports the idea that anthracene arises following ortho attack of benzyl on toluene or on a benzyl radical. The following mechanism is a modification of that put forward by Errede.[19]



If the above explanations for phenanthrene and anthracene were the only mechanisms operating, then activities of these compounds should have been 2.64 μc. per millimole instead of 2.26 or 2.52. From this, one could assume that 85.6% of the phenanthrene and 95.5% of the anthracene came as indicated, but that 14.4 and 4.5%, respectively, must have come by some pathway not leading to radioactivity. It is reasonable to assume that some of the phenanthrene and a lesser part of the anthracene came by diene addition of II to the essentially non-radioactive naphthalene, followed by dehydrogenation

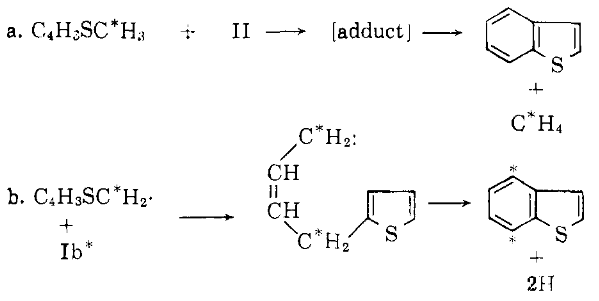


This gain of phenanthrene and anthracene at the expense of naphthalene no doubt is typical of other reactions occurring in the hot system, for the anthracene and phenanthrene may be similarly depleted as they change into tetracyclic systems, and so on. This would explain the large amount of tar that was observed.

Tracer methods were used similarly on 2-(methyl-^{14}C)-thiophene, having an activity of 1.28 μc./mmole. These products were found after pyrolysis: benzene (as *m*-dinitrobenzene), 2.34 μc./mmole; benzothiophene (as its 1,1-dioxide), 0.90 μc./mmole; naphthalene, 1.35 μc./mmole.

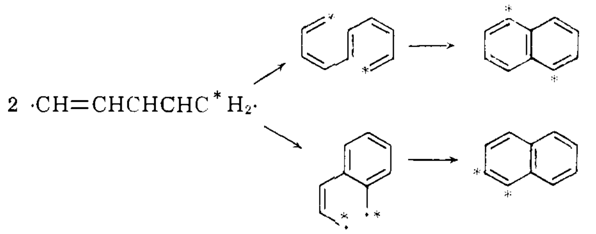
The activity of the benzene was nearly twice that of the starting material, indicating the presence of two ^{14}C atoms per molecule. This substantiates the hypothesis that fragment I is formed, which dimerizes: $C_4H_3SC^*H_2\cdot \rightarrow Ia^*(\text{or } Ib^*) \rightarrow C_6{}^{**}H_6$. A much smaller quantity of benzene without radioactivity would come *via* the formed thiophene (see above): $C_4H_3SC^*H_3 + H\cdot \rightarrow C_4H_4S + C^*H_4$. This explains why the observed activity of the benzene was 2.34 μc. rather than 2.56 μc.

Just as two routes were indicated for the formation of naphthalene from toluene, so also they are in the formation of benzothiophene from 2-methylthiophene



Route a was followed to the extent of 65% and route b 35%, based on the radioactivity. That route a was lower for methylthiophene yielding benzothiophene than for toluene yielding naphthalene (65 *vs.* 91%) is reasonable in view of the fact that radical II is formed indirectly from methylthiophene *via* thiophene, whereas it is formed directly from toluene.

More work is required before the origin of the naphthalene from 2-methylthiophene can be explained satisfactorily. A naphthalene with two ^{14}C atoms/molecule is easy to visualize by way of the C_5H_6 moiety (see above). A small amount of



the same could come by diene addition of II to $C_6{}^{**}H_6$.

$$C_4H_3S\text{—}C^*H_3 \begin{cases} \nearrow Ia^* \longrightarrow C_6{}^{**}H_6 \\ \searrow C_4H_4S \longrightarrow II \end{cases}$$

$$C_6{}^{**}H_6 + II \longrightarrow C_{10}{}^{**}H_8 + H_2$$

This kind of naphthalene would require 2.56

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

BY CHARLES D. HURD, ROBERT V. LEVETAN[1a] AND A. R. MACON[1b]

RECEIVED MARCH 12, 1962

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

(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).