[CONTRIBUTION NO. 168 FROM THE CENTRAL RESEARCH LABORATORIES OF MINNESOTA MINING AND MANUFACTURING CO.[1]]

The Chemistry of Xylylenes. V. The Formation of Anthracenes *via* Fast Flow Pyrolysis of Toluenes and Related Compounds[2]

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Anthracenes are obtained in 60–90% conversion per pass when *o*-methylated diarylmethanes are subjected to fast flow pyrolysis at low pressure. A mixture of diarylmethanes and anthracenes is obtained when bibenzyls are subjected to the same reaction conditions; the fast flow pyrolysis of toluenes affords mixtures of bibenzyls, diarylmethanes and anthracenes. The results are consistent with a stepwise mechanism for thermal conversion of benzyl radicals to anthracenes *via* bibenzyls and *o*-methylated diarylmethanes as pyrolysis intermediates.

Introduction

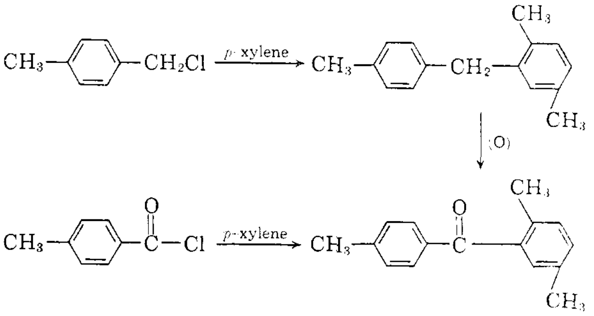
It has been known for many years that anthracenes are formed in small amounts when toluene or other alkylbenzenes are pyrolyzed at atmospheric pressure.[4] Unfortunately, the reaction conditions are so severe that extensive rupture of the aromatic ring occurs and the pyrolyzate is an intractable complex mixture that offers little or no clue to the mechanistic sequence of reactions leading ultimately to the formation of anthracene. More recently,[5,6] however, it has been observed that these compounds are also produced when toluenes are subjected to the relatively mild conditions of fast flow pyrolysis at low pressure. Since thermal rupture of the aromatic nuclei does not occur significantly under these conditions,[6] the complexity of the pyrolyzate is markedly lessened and, correspondingly, the data are more amenable to interpretation.

Results and Discussions

The fast flow pyrolysis of toluene and *p*-xylene at low pressure was re-investigated quantitatively, and material balances carried out in this study accounted for 98 ± 4% of the phenyl groups metered to the pyrolysis system so long as the pressure did not exceed 10 mm. Hydrogen and methane were the only non-condensable gases produced in significant amounts as determined by mass spectrometric analysis. Thus, for example, when toluene was pyrolyzed at 970°, 0.5 mm. pressure and 0.002 sec. residence time, 0.3% of the feed stock was converted to bibenzyl, 0.1% to benzene, 0.05% to ethylbenzene, 0.09% to diphenylmethanes, and 0.05% to anthracene and 96% was recovered as unreacted toluene.[7] Similarly, fast flow pyrolysis of *p*-xylene at 1065°, 4 mm. pressure and 0.004 sec. residence time converted 12% of the feed stock to *p*-xylylene, 7% to toluene, 2% to styrene, 1% *p*-ethyltoluene, 0.7% 1,2-di-*p*-tolylethane, 0.7% diarylmethanes,[8] 0.3% anthracenes, 0.3% 4,4′-dimethylstilbene, and 76% was recovered as unreacted *p*-xylene.

Although the exact amount of each component in the product mixture varies markedly with the reaction conditions,[9] the consistent presence of significant quantities of bibenzyls and diarylmethanes in the above pyrolyzates is sufficient reason for considering whether or not these compounds are intermediates in a possible stepwise formation of anthracenes from toluenes as postulated in Fig. 1. Thus, thermal rupture of methyl C–H bonds affords benzyl radicals that couple to form bibenzyls.[6] The latter is a reversible reaction[5] and eventually recombination occurs irreversibly (perhaps on the reactor wall) affording *o*-methylated diarylmethanes. These in turn can undergo dehydrogenation to yield anthracenes as stable end products. Demethylation of *o*-methylated diarylmethanes and coupling of benzyl radical intermediates with methyl radicals affording diarylmethanes with no *o*-methyl substituents and ethylbenzenes, respectively, are two side reactions that decrease the yield of anthracenes. The pyrolysis of *p*-xylene is complicated even further by conversion of *p*-methylbenzyl radicals to *p*-xylylene.[10]

To test whether or not fast flow pyrolysis of *o*-methylated diarylmethanes would afford the corresponding anthracenes in good yield, it was first necessary to synthesize the series of model compounds listed in Table I. These were prepared in 65–90% yield by dropwise addition of a benzyl halide to an excess of the appropriate alkylbenzene containing a catalytic amount of $AlCl_3$ as described in the Experimental section. The assigned structures were verified by their infrared spectra, nuclear magnetic resonance spectra, elemental analyses and molecular weights. The identity of *p*-tolyl-*p*-xylylmethane was confirmed by oxidation to 2,5,4′-



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[1] Most of this work was carried out in the laboratories of The M. W. Kellogg Co. The data were acquired by Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Co. in March, 1957.

[2] Presented before the Organic Division of the American Chemical Society at its 136th Meeting in Atlantic City, N. J., September, 1959.

[3] The M. W. Kellogg Co., Jersey City, N. J.

[4] C. D. Hurd, "The Pyrolysis of Carbon Compounds," (The Chemical Catalog Co.) Reinhold Publ. Corp., New York, N. Y., 1929.

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

[6] (a) M. Szwarc, *Nature*, **160**, 403 (1947); (b) I. Tanaka and S. Inowaki, *J. Chem. Soc. Japan*, **75**, 609 (1954).

[7] L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, **24**, 1890 (1959).

[8] Although the products obtained when *p*-xylene is subjected to fast flow pyrolysis were reported previously by others[5,6] the formation of diarylmethanes somehow was overlooked and is reported here for the first time.

[9] L. A. Errede and F. DeMaria, unpublished results.

[10] M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

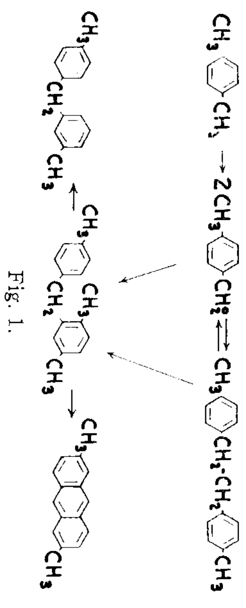

Fig. 1.

trimethylbenzophenone which also was prepared *via* interaction of *p*-toluyl chloride with *p*-xylene in the presence of $AlCl_3$.

Similarly, oxidation of diphenylmethane and *p*-tolyl-*m*-tolylmethane afforded the corresponding known benzophenones.[11] These results proved that the pyrolysis feed stocks were at least 90% pure with respect to the assigned structures and we considered this degree of purity adequate for our study.

The *o*-methylated diarylmethanes were pyrolyzed at 970° and 0.03 sec. residence time and the corresponding anthracenes were produced in high conversion and good yield (see Table II). Thus, anthracene was obtained in 91% conversion/pass from *o*-benzyltoluene; 2-methylanthracene was obtained in 64–86% conversion per pass from the 6-benzyl-*m*-xylene, *p*-tolyl-*o*-tolylmethane and 2-benzyl-*p*-xylene, and finally 2,6-dimethylanthracene was obtained in 55% conversion per pass from *o*-tolyl-*p*-xylylmethane. No anthracene or its derivative was obtained when diphenylmethane, *m*-tolyl-*p*-tolylmethane or di-*p*-tolylmethane was pyrolyzed using the same experimental conditions proving that ring closure involves the *o*-methyl substituent. In the latter two instances, small amounts of polymeric material were obtained and their infrared spectra were similar to that of poly-*p*-xylylene. Each anthracene was identified by its melting point, characteristic fluorescence when irradiated with ultraviolet light (purple for anthracene, yellow-green for 2-methylanthracene and pale blue for 2,6-dimethylanthracene) and by conversion to its corresponding anthraquinone by oxidation with $K_2Cr_2O_7$ in acetic acid.

The percentage conversion of pyrolysis feed stock to anthracene is decreased to 3–16% when bibenzyls are used in place of *o*-methylated diarylmethanes. Thus the fast flow pyrolysis of bibenzyl at 940° afforded a mixture of diarylmethanes, *trans*-stilbene and anthracene in 2, 11 and 16% conversion, respectively. Infrared analysis indicated that the diarylmethanes were diphenylmethane and *o*-benzyltoluene. Similar results are obtained with 1,2-di-*p*-tolylethane although this reaction is complicated further by the formation of *p*-xylylene from the intermediate *p*-methylbenzyl radical produced *via* C–C rupture of the ethylene bridge.[5]

The isolation of diarylmethanes as well as anthracenes in respectable yields is evidence that bibenzyls rearrange thermally to *o*-methylated diarylmethanes which in turn can undergo demethylation or anthracene formation. Demethylation increases with increase in severity of the reaction conditions which modifies the product distribution accordingly. Actually anthracene formation is favored at the

Table I

Synthesis of Diarylmethanes

Benzyl halide	Solvent	Diarylmethane produced	Yield, %	B.p., °C. (mm.)	M.p., °C.	Density (23°)	n_D (t, °C.)		Elemental analyses C, %	H, %	Mol. wt.	N.m.r. spectra (Ar–H)	(CH_2)	(CH_3)	Infrared spectra, mμ *ortho*	*meta*	*para*	mono
o-Methylbenzyl bromide	Benzene	*o*-Benzyltoluene	71	97–98	0–4	0.9985	1.5757	Calcd.	92.26	7.74	182.3	2.85	6.07	7.79	13.62s	.....	.....	13.62s
				(0.8)			(20)	Found	92.8	7.42	179	2.95						
p-Methylbenzyl bromide	Toluene	Di-*p*-tolylmethane^a and	91	118–120	23.5–	....	1.5651					3.04^a	5.19^a	7.73^a				
		o-tolyl-*p*-tolylmethane^b		(1)	26.5^a		(20)								13.68s^b	.....	12.65s^b	....
Benzyl chloride	*m*-Xylene	6-Benzyl-*m*-xylene	67	139–142	....	....	1.5678	Calcd.	91.83	8.22	196.3	2.93	6.20	7.83		11.45m	12.05	13.78
				(1.2)			(22)	Found	91.8	8.25	199	3.12		7.71		13.01m		14.40
Benzyl chloride	*p*-Xylene	*o*-Benzyl-*p*-xylene	73	127–128	....	....	1.5697	Calcd.	91.83	8.22	196.3	2.85	6.12	7.83		11.35m	12.41s	13.78s
				(1.5)			(22)	Found	91.4	8.44	200	3.09		8.29		13.05w		14.42s
o-Methylbenzyl bromide	Toluene	*m*-Tolyl-*p*-tolylmethane^c	89	112–114	....	0.9950	....		...	..	...	...	...	...	13.58w	11.38m	12.58s	....
		o-tolyl-*p*-tolylmethane		(0.7)												12.97s		
		di-*o*-tolyl-*p*-tolylmethane														14.44s		
p-Methylbenzyl chloride	*p*-Xylene	*p*-Tolyl-*p*-xylylmethane	82	136–143	....	0.9722	1.5645	Calcd.	91.37	8.62	210.3	3.05	6.20	7.73		11.34m	12.40s	....
				(2)			(23)	Found	91.6	8.44	213	3.12		7.88		13.12m		
																14.35w		

[a] Di-*p*-tolylmethane was isolated from mixture by crystallization from methanol at −15°. Sample of compound was oxidized to di-*p*-tolyl ketone (m.p. 91.5–92.5°) which was then converted to its 2,4-dinitrophenylhydrazone (m.p. 223–225°). [b] Impure *o*-tolyl-*p*-tolylethane was isolated from methanol mother liquor. [c] Infrared spectrum indicated that the mixture was mostly *m*-tolyl-*p*-tolylmethane. Experiment was repeated and again a mixture was obtained although this time *o*-tolyl-*p*-tolylmethane was a major product. [d] Strong absorption, (m) medium absorption, (w) weak absorption.

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(11) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Publishing Co., London, 1956, p. 1063.

TABLE II

PYROLYSIS OF DIARYLMETHANES

Diarylmethane	Anthracene obtained	Yield per pass, %	M.p., °C.	Color of anthracene		Quinone derivative	M.p. °C.
				Ordinary light	U.v. light		
o-Benzyltoluene	Anthracene	91	202–206	White	Purple	Anthraquinone	289–291
o-Tolyl-*p*-tolylmethane[a]	2-Methylanthracene	>50[a]	206–207	Pale yell.	Bright yell.-green	2-Methylanthraquinone	176–177
6-Benzyl-*m*-xylene	2-Methylanthracene	86	198–201	Pale yell.	Bright yell.-green	2-Methylanthraquinone	176–177
o-Benzyl-*p*-xylene	2-Methylanthracene	64	200–202	Pale yell.	Bright yell.-green	2-Methylanthraquinone	176–177
p-Tolyl-*p*-xylylmethane	2,6-Dimethylanthracene	55	227–230	Green.-yell.	Pale blue	2,6-Dimethylanthraquinone	240–242
Di-*p*-tolylmethane	None	..	.....	....	....	....	.....
p-Tolyl-*m*-tolylmethane	None	..	.....	....	....	....	.....
Diphenylmethane	None	..	.....	....	....	....	.....

[a] Starting material was contaminated with unknown amount of di-*p*-tolylmethane.

TABLE III

PYROLYSIS OF TOLUENES AND BIBENZYLS

Compound pyrolyzed	Pyrolysis conditions			Product distribution, % conversion per pass		
	T, °C.	P, mm.	t, sec.	Bibenzyls	Diarylmethanes	Anthracenes
Toluene	970	0.5	0.002	0.3[a]	0.09[b]	0.05[c]
Toluene	970	5.0	.02	1.1[a]	.4[b]	.2[c]
p-Xylene	1065	4.0	.004	0.7[d]	.7[e]	.3[f]
p-Xylene	915	20	.03	1.0[d]	.4[e]	.1[g]
Bibenzyl	940	1.0	.04	..	2.0[b]	16.0[c]
1,2-Di-*p*-tolylethane	970	1.0	.003	..	3.0[h]	6.0[g]
1,2-Di-*p*-tolylethane	1000	3.5	.04	..	6.9[e]	2.9[f]
1,2-Di-*p*-tolylethane	1000	4.0	.25	..	5.0[e]	2.4[f]

[a] Bibenzyl. [b] *o*-Benzyltoluene. [c] Anthracene. [d] 1,2-Di-*p*-tolylethane. [e] Mixture of diarylmethanes. [f] Mixture of anthracenes. [g] 2,6-Dimethylanthracene. [h] *p*-Tolyl-*p*-xylylmethane, major component.

lower range of pyrolysis temperatures. If the pyrolysis conditions are too mild, however, neither diarylmethanes nor anthracenes are obtained. Thus the pyrolysis of 1,2-di-*p*-tolylethane at 730° by Schaefgen[5] afforded *p*-xylylene, *p*-xylene, hydrogen, methane, ethylene, ethane, *p*-ethyltoluene, *p*-vinyltoluene, toluene and 4,4′-dimethylstilbene but no diarylmethanes or anthracenes.

The results of the experiments described above are summarized in Tables II and III and it is noted that the percentage conversion to anthracene increases from about 0.2% to about 10% to about 70% when toluenes, bibenzyls and *o*-methylated diarylmethanes, respectively, are subjected in turn to the same conditions of fast flow pyrolysis. Moreover pyrolysis of each affords all the corresponding subsequent intermediate compounds noted in the proposed reaction sequence. These results are consistent with a mechanism that involves a stepwise formation of anthracenes from toluenes as outlined in Fig. 1.

o-Xylene deserves especial comment. It was reported by Szwarc[10] that anthracene in about 13% conversion per pass is obtained as the major product instead of the expected *o*-xylylene when *o*-xylene is subjected to fast flow pyrolysis as described above and that methane and hydrogen are produced in equal amounts. These observations were reconfirmed in our laboratory. If relatively mild conditions of pyrolysis are used, however, 1,2-di-*o*-tolylethane is obtained as the major product and this can be converted by pyrolysis to anthracene. This suggests that *o*-methylbenzyl radical intermediates are particularly prone to undergo aromatic substitution to afford anthracene. Thus collision of two *o*-methylbenzyl radicals would result in ring closure with simultaneous expulsion of methane as indicated in Fig. 2.

Experimental

Pyrolysis of *p*-Xylene.—*p*-Xylene was pyrolyzed at 1065 ± 5°, 4.0 ± 0.1 mm. pressure and 0.0041 ± 0.0003 sec. residence time and the pyrolyzate was condensed in 4 liters of hexane kept at −78°. The details of this procedure are described in a previous publication.[12] A *p*-xylylene concentration of 0.08 to 0.12 mole/liter was accumulated after 3 hours of pyrolysis. *p*-Xylylene is an extremely reactive molecule even at −78°.[12] Its half-life in solution at −78° is 22 hours, whereas it is less than a second at 23°. The solution was warmed to room temperature thereby forcing rapid polymerization of all the accumulated *p*-xylylene. A copious precipitate of poly-*p*-xylylene formed throughout the liquid and this was removed by filtration.

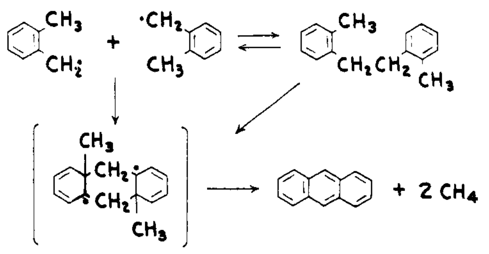

Fig. 2.

Mass spectrometric analysis of the hexane mother liquor indicated that toluene, benzene, styrene and *p*-ethyltoluene were produced during the pyrolysis and had been condensed along with *p*-xylene. The compounds were identified primarily by their respective molecular mass peaks and secondarily by their corresponding characteristic fragmentation patterns.[13] In this respect some data indicated that cycloöctatetraene might also be present in the pyrolyzate in small amount, but this was not confirmed by other methods of identification. An appreciable amount of styrene was accumulated in the liquid nitrogen trap of the pyrolysis system. Its presence in the condensate mixture was indi-

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(12) L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

(13) The fragmentation patterns of sample compounds, including the molecules considered here, are given in the American Petroleum Institute Mass Spectra Data Sheets.

cated clearly by its infrared absorption spectrum, showing peaks at 10.1, 11.05, 12.9 and 14.4 μ, and by its characteristic odor. No attempt was made to isolate these volatile compounds in pure form nor to prepare solid derivatives thereof since these compounds were reported previously by others[5,6] and were of no real interest to us except to verify that they were being formed as side products and therefore required a satisfactory method for their quantitative detection.

Mass spectrometric analysis of the hexane mother liquor was the method of choice because of convenience since, at the time, this instrument was available in the Petroleum and Chemical Laboratories of the M. W. Kellogg Co., as a routine service for quantitative analysis of comparable hydrocarbon mixtures whereas gas chromatography was not.

The soluble non-volatile products of pyrolysis (1,2-di-*p*-tolylethane, di-arylmethanes and anthracenes) and the soluble products of *p*-xylylene polymerization (cyclo-di, tri- and tetra-*p*-xylylene and low molecular weight poly-*p*-xylene) were recovered by evaporation of the hexane mother liquor. The combined weight of insoluble polymer and soluble residue was considered simply as "xylyl equivalents" without attempting to differentiate the components of the mixture at this stage of the analysis.

A series of 10 experiments using the pyrolysis conditions given above indicated that the analytical procedure accounted for 99 ± 3% of the phenyl units metered to the system as *p*-xylene and that the composition of the condensate was 76 ± 2% *p*-xylene, 14 ± 1% "xylyl equivalents," 7.1% toluene, 2 ± 0.6% styrene and 1 ± 0.5% *p*-ethyltoluene.

In order to determine the actual composition of the non-volatile products tentatively considered as "xylyl equivalents," additional runs were carried out at the specified conditions of pyrolysis until a total of 2.5 kg. of insoluble polymer and 2.3 kg. of soluble non-volatile products was accumulated as described above. The infrared spectrum (strong peak at 12.20μ, medium at 8.30, 8.78, 9.26 and 9.81μ plus the usual aromatic peaks at 3 to 7.5μ) and X-ray diffraction pattern (sharp rings at 4.0 and 5.3 Å.) of the insoluble polymer indicated that this material was the α-form of poly-*p*-xylylene as characterized by Brown and Farthing.[14] The linear configuration of this polymer was verified when terephthalic acid was the only isolatable product of the polymers when oxidized by $K_2Cr_2O_7$ in acetic acid. This is in agreement with the results reported previously by Brown and Farthing.[14]

The semi-solid mixture of soluble non-volatile products (2292 g.) was washed with a vigorous stream of hexane leaving a residue of insoluble heavy crystals of cyclo-di-xylylene (20 g.). The compound was purified by recrystallization from toluene in the form of cubic crystals (m.p. 281–283°).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.29; H, 7.74; mol. wt., 208. Found: C, 92.4; H, 7.58; mol. wt., 206.

The nuclear magnetic resonance spectrum[15a] (τ 3.61 for phenyl, 7.01 for methylene) is consistent with the assigned structure and the infrared spectrum is identical with that reported in the literature.[15b]

The hexane slurry of insoluble fluffy products from the above washing was separated by filtration. The average molecular weight of this dark brown insoluble material (701 g.) was 1020 to 1600 (cryoscopic method in benzene). The infrared spectrum was similar to that of insoluble poly-*p*-xylene. On the basis of these results it was concluded that this material is mostly low molecular weight poly-*p*-xylylene.

The filtrate was separated by chromatography to yield 575 g. of white crystals (m.p. 135–150°) and 692 g. of a non-volatile amber oil. This was accomplished by using four columns, 6 feet long and 2 inches in diameter, each filled with 4 lb. of active alumina. Each column was eluted with 22 liters of hexane and successive 1-liter cuts were taken. The residual adsorbed material was eluted by progressively polar solvents in the usual fashion. The non-volatile solid residue from each cut was recrystallized from methanol and was obtained in two distinct crystalline forms. One was large and dense and the other was small and fluffy. The crystals were separated easily by swirling and decantation. The small fluffy needles (28 g.) were recrystallized from ethanol in the form of tiny pearl-white platelets (m.p. 140.5–142°). The infrared spectrum of this compound (strong peak at 12.24μ for *para* substituents, weak peak at 7.25μ for methyl, plus the usual aromatic and aliphatic absorptions from 3.0 to 7.0μ) and its melting point are in agreement with those reported for 1,4-bis-(2-*p*-tolylethyl)-benzene.[16] The assigned structure also was verified by its proton magnetic resonance spectrum (τ-values: 3.01 for phenyl, 7.19 for methylene and 7.70 for methyl). The large heavy needles (515 g.) were recrystallized from acetone to yield large pinate crystals (m.p. 162–164°). A small sample was purified further by sublimation. The melting point (166–167°) and infrared spectrum of this compound are in agreement with those reported for cyclo-tri-*p*-xylylene.[16,17] Its proton magnetic resonance spectrum (τ-values: 3.40 for phenyl and 7.08 for methylene) was also consistent with the assigned structure.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.29; H, 7.74; mol. wt., 312. Found: C, 91.9; H, 8.07; mol. wt., 299.

The acetone mother liquor was concentrated to a small fraction of its original volume and crystallization was allowed to occur very slowly. A few large crystals formed along with the needle-like crystals of cyclo-tri-*p*-xylylene. The former were removed by means of a pair of tweezers and then purified by recrystallization from acetone. The compound (m.p. 179–182°) was identified as cyclo-tetra-*p*-xylylene since its molecular weight was found to be 421 and its infrared spectrum is very similar to that of poly-*p*-xylylene. Its proton magnetic resonance spectrum (τ-values: 3.37 for phenyl and 7.22 for methylene) is also in agreement with the assigned structure.

The 692 g. of amber oil was separated by vacuum distillation at 1 mm. pressure into three fractions: (1) 501 g., b.p. 112–140°; (2) 115 g., b.p. 160–200°; (3) 50 g. residue. Infrared analysis indicated that fraction 3 was mostly cyclo-tri-*p*-xylylene and that fraction 2 was a mixture of anthracenes from which anthracene (m.p. 214–215°, purple fluorescence under ultraviolet light), 2-methylanthracene (m.p. 206–207°, yellow green fluorescence under ultraviolet light) and 2,6-dimethylanthracene (m.p. 239–241°, pale blue fluorescence under ultraviolet light) were separated by repeated fractional crystallization and sublimation. A sample of each anthracene was oxidized by $K_2Cr_2O_7$ in hot acetic acid to anthraquinone (m.p. 289–291°), 2-methylanthraquinone (m.p. 176–177°) and 2,6-dimethylanthraquinone (m.p. 240–243°), respectively. Although the separation of the anthracene mixture was by no means quantitative, the major component appeared to be 2-methylanthracene.

Fraction 1 was dissolved in a minimum amount of methanol, and the solution was cooled to −78°). Tiny platelets of 1,2-di-*p*-tolylethane (242 g., m.p. 74–76°) precipitated from solution; a 3-g. sample of the crystalline hydrocarbon was purified further by sublimation and subsequent final recrystallization from hexane to afford the compound in the form of pearl-white platelets (m.p. 80.5–81.5°). Its nuclear magnetic resonance spectrum (τ-values: 3.04 for phenyl, 7.19 for methylene, 7.78 for methyl) is consistent with the assigned configuration.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63; mol. wt., 210.3. Found: C, 91.4; H, 8.48; mol. wt., 206.

The solute of the methanol mother liquor was recovered by evaporation to constant weight (250 g.) at 100°. The oil was redistilled at 0.06 mm. pressure (b.p. 82–83°, $n^{23}D$ 1.5670). The ultraviolet and infrared spectra of the center cut and its elemental analysis indicated that the oil was a mixture of dimethyl homologs of diphenylmethane.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22; mol. wt., 196.3. Found: C, 91.8; H, 8.36; mol. wt., 187.

Thus the composition of the 4.8 kg. of non-volatile product produced *via* fast flow pyrolysis of *p*-xylene at 1065°, 4 mm. pressure and 0.004 sec. residence time was 80% *p*-xylylene (isolated as its products of polymerization;

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(14) C. J. Brown and A. C. Farthing, *J. Chem. Soc.*, 3276 (1953).

(15) (a) The nuclear magnetic resonance τ-values reported here refer to the system of G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958); the melting points reported here are all uncorrected; (b) D. J. Cram and H. Steinberg. THIS JOURNAL, **73**, 5691 (1951).

(16) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(17) L. A. Auspos, C. W. Burman, L. A. R. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. P. Speck, *J. Polymer Sci.*, **15**, 19 (1955).

2.5 kg. of insoluble polymer, 700 g. of soluble polymer, 600 g. of cyclo-tri-*p*-xylylene and 20 g. of cyclo-di-*p*-xylylene), 5% di-arylmethanes, 5% *sym*-di-*p*-tolylethane, 2% anthracenes and 8% unaccounted for material. These results enable one to break down the observed 14% conversion of *p*-xylene to non-volatile products (weighed initially as "xylyl equivalents") into 12% *p*-xylylene, 0.7% *sym*-di-*p*-tolylethane, 0.7% diarylmethanes and 0.3% anthracenes.

The composition of the pyrolyzate produced *via* fast flow pyrolysis is a function of the pyrolysis conditions. Thus in another series of experiments in which 32 kg. of *p*-xylene was pyrolyzed at 900 to 930°, 0.01 to 0.04 sec. residence time and 10 to 30 mm. pressure, there was accumulated 1 kg. (3.1% yield) of non-volatile products. This mixture was separated essentially as described above. The composition was 49.5% *p*-xylylene (isolated as its product of polymerization), 31% *sym*-di-*p*-tolylethane, 13% diarylmethanes, 3% anthracenes (mostly 2,6-dimethylanthracene) and 2% 4,4'-dimethylstilbene. Thus, these products were obtained in 1.5, 1.0, 0.4, 0.1 and 0.05% conversion per pass, respectively.

Pyrolysis of Toluene.—Chemically pure toluene (b.p. 110–111°) purchased from Merck & Co., Inc., was used as the pyrolysis feed stock. Gas chromatography and infrared analysis indicated that its composition was 99.8% toluene, 0.1% benzene and 0.1% aliphatic hydrocarbon. Five hundred grams of this feed stock (5.4 moles) was vaporized and subjected to fast flow pyrolysis at 970°, 0.5 mm. pressure and 0.002 sec. residence time using the pyrolysis system described previously.[12] The pyrolyzate was condensed at −78° and then separated by distillation at atmospheric pressure. The mixture of volatile components (480 g., b.p. <140°) was analyzed by gas chromatography and infrared analysis and its composition was found to be 98.9% toluene, 0.7% benzene, 0.4% ethylbenzene, <0.1% aliphatic hydrocarbon and a trace amount of xylene. The non-volatile residue (2.3 g., b.p. <140°) was analyzed by infrared analysis and then separated into its components using vacuum distillation and recrystallization as described previously.[8] Its composition was 70% bibenzyl, 20% diarylmethanes and 10% anthracene. The diarylmethanes were identified qualitatively by infrared analysis as diphenylmethane and *o*-benzyltoluene. A small amount of stilbene also was detected. Thus 5.4 moles of toluene were metered to the system and 5.1 moles were recovered; the rest was converted to 0.04 mole of benzene, 0.007 mole of bibenzyl, 0.002 mole of diarylmethanes and 0.001 mole of anthracene. Consequently the conversion of toluene to bibenzyl, diarylmethane and anthracene is 0.3, 0.09 and 0.05%, respectively. The pyrolysis was repeated at 970°, 5 mm. and 0.02 sec. residence time and these conversions per pass were increased to 1.1, 0.4 and 0.2%, respectively.

Preparation of Diarylmethanes.—The benzyl halide (0.33 mole) dissolved in 1 liter of the aromatic solvent was added dropwise over a period of 2 hours to a stirred suspension of 5.5 g. of $AlCl_3$ in 2.5 liters of aromatic solvent kept at 80–90°. Reaction was allowed to occur for an additional hour before the mixture was cooled to room temperature and then extracted with water. The excess organic solvent was removed by distillation at 100 mm. The diarylmethane obtained as residue was purified by distillation at 1–2 mm. The structure of the anticipated diarylmethane was checked by infrared analysis, nuclear magnetic resonance and elemental analysis. The data are summarized in Table I.

2,5,4'-Trimethylbenzophenone.—*p*-Tolyl-*p*-xylylmethane (3 g.), prepared *via* Friedel–Crafts reaction as described above, was oxidized by 3 g. of $K_2Cr_2O_7$ in 50 cc. of hot acetic acid to yield 2.5 g. of 2,5,4'-trimethylbenzophenone (b.p. 140–144° (1.4 mm.)). The oil solidified slowly and was recrystallized from methanol in the form of white platelets (m.p. 45.5–47.0°).

Anal. Calcd. for $C_{16}H_{18}O$. C, 85.67; H, 7.17. Found: C, 85.7; H, 7.09.

The ketone was also prepared in *ca.* 60% yield *via* addition of 20 g. of *p*-toluyl chloride to excess *p*-xylene in the presence of catalytic amounts of $AlCl_3$. The reaction mixture was worked up in the usual fashion to afford 2,5,4'-trimethylbenzophenone (m.p. 46.0–47.0°; no depression observed when this sample mixed with above ketone). A sample of each was converted to the same 2,4-dinitrophenylhydrazone *via* reaction with 2,4-dinitrophenylhydrazine according to the directions of Shriner and Fuson.[18] The compound was recrystallized from a solution of methyl alcohol and ethyl acetate and was obtained in the form of orange platelets (m.p. 255.5–257.5°).

Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 65.34; H, 4.99; N, 13.85. Found: C, 65.1; H, 4.89; N, 14.1.

4,4'-Dimethylbenzophenone from Di-*p*-tolylmethane.—A mixture of *o*-tolyl-*p*-tolylmethane and di-*p*-tolylmethane (b.p. 118–120° (1 mm.), n^{20}D 1.5651) was obtained in 91% yield when *p*-methylbenzyl chloride was made to react with toluene as described above. The mixture was dissolved in methanol and then kept at −15° for several days. Di-*p*-tolylmethane[11] (m.p. 23.5–26.5°; τ-values: 3.04 for phenyl, 6.19 for methylene, 7.73 for methyl) crystallized slowly from the cold solution and was removed by filtration at −15°. The assigned structure was verified by oxidation of a sample by $K_2Cr_2O_7$ in hot acetic acid to afford di-*p*-tolyl ketone (m.p. 91.5–92.5°)[11] and subsequent conversion to its 2,4-dinitrophenylhydrazone (m.p. 223–225°).

3,4'-Dimethylbenzophenone from *m*-Tolyl-*p*-tolylmethane.—A mixture of di-tolylmethanes (b.p. 112–114° (0.7 mm.), n^{20}D 1.5602, density 0.995) was obtained in 89% yield when *o*-methylbenzyl bromide was made to react with toluene as described above. The infrared spectrum indicated that the product was mostly *m*-tolyl-*p*-tolylmethane (medium peak at 11.38μ, strong peaks at 12.97 and 14.44μ indicating *meta* and strong peak at 12.88μ indicating *para*) and that the expected *o*-tolyl-*p*-tolylmethane (band at 13.58μ) was present in relatively minor amounts. Apparently considerable rearrangement had occurred. An aliquot sample of the mixture was oxidized by $K_2Cr_2O_7$ in acetic acid and 3,4'-dimethylbenzophenone (m.p. 79–81°)[11] was isolated as the major product. This was converted to its corresponding 2,4-dinitrophenylhydrazone (m.p. 208–211°).

Pyrolysis of Diarylmethanes.—The diarylmethane (25 g.) was metered in the liquid state at the rate of 0.001 mole per minute into the pyrolysis system evacuated to 1 mm. pressure. The compound was vaporized at 176° and the gas stream was pyrolyzed at 970° and 0.03 sec. residence time using a 1 inch i.d. quartz tube. The pyrolyzate was condensed at −78°. At the end of the experiment the condensate was leached at room temperature with hexane and the residue was weighed as anthracene. The residual anthracene was purified further by sublimation and subsequent recrystallization from methanol. The anthracene obtained was identified by its m.p., color and infrared spectrum and by converting a sample to its corresponding anthraquinone by oxidation with $K_2Cr_2O_7$ in hot acetic acid. A mixture of unreacted starting material and demethylated

TABLE IV

PYROLYSIS OF 1,2-DI-*p*-TOLYLETHANE

Pyrolysis conditions			
1,2-Di-*p*-tolylethane used, mole	0.275	0.205	0.240
Temperature of pyrolysis, °C.	1000	970	1000
Residence time in seconds	0.041	0.003	0.25
Pressure, mm.	3.5	1	4.0
1,2-Di-*p*-tolylethane recovd., mole	....	0.10[a]	0.067[a]
Product distribution, % conversion			
Poly-*p*-xylylene	5.5	11	8.3
p-Xylene	..	8	7.1
Diarylmethanes[b]	6.9	3[c]	5.0
Anthracenes[d]	2.9	6	2.4
p-Ethyltoluene	..	1	0.6
p-Methylstyrene	..	1	0.6
Toluene	..	0.5	1.1
Styrene	..	Trace	0.5

[a] Presence of 4,4'-dimethylstilbene detected by infrared analysis. [b] Presence of *p*-tolyl-*p*-xylylmethane detected by infrared analysis. [c] Product mostly *p*-tolyl-*p*-xylylmethane. [d] Product mostly 2,6-dimethylanthracene.

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[18] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

diarylmethane was recovered by evaporating the hexane extract to constant weight. Identification of these products was made by infrared spectrometric analysis. The results are summarized in Table II

Pyrolysis of Bibenzyls.—(a) Bibenzyl (57.1 g., m.p. 49–50°) was evaporated at 100° and 1 mm. pressure and the vapor stream was pyrolyzed at 940° and 0.04 sec. residence time. The pyrolyzate was condensed at −78° and this was subsequently separated by distillation to afford 1.2 g. (2% yield) of phenyl-*o*-tolylmethane (b.p. 70–75° (0.5 mm.)); 6.3 g. (11% yield) of *trans*-stilbene (b.p. 85–90° (0.5 mm.), m.p. 124°) and 9.1 g. (16% yield) of anthracene (b.p. <90° (0.5 mm.), m.p. 210–212°).

(b) **4,4'-Dimethylbibenzyl (1,2-Di-*p*-tolylethane).**—1,2-Di-*p*-tolylethane (57.8 g., m.p. 79–80°) was vaporized at low pressure and the gas stream was subjected to fast flow pyrolysis. The pyrolyzate was leached with ether. The extract was separated by distillation at atmospheric pressure. The distillate boiling in the range 60–140° was analyzed quantitatively by gas chromatography and the components were identified by mass spectrographic and infrared analysis as benzene, toluene, *p*-xylene, styrene, *p*-ethyltoluene and *p*-methylstyrene. Others[5,19,20] have also reported that these compounds are produced when 1,2-di-*p*-tolylethane and related products are subjected to pyrolysis at low pressure. The ether-insoluble residue was leached with hot toluene and this residue was identified as poly-*p*-xylylene. The toluene extract was evaporated to dryness and admixed with the previous material whose boiling point at atmospheric pressure was greater than 140°. This mixture was separated by distillation under vacuum and subsequent recrystallization as described above. The components were identified by their corresponding m.p. and infrared spectra as unreacted starting material, diarylmethanes, anthracenes and stilbenes. The results are summarized in Table IV.

Pyrolysis of *o*-Xylene.—(a) *o*-Xylene was pyrolyzed at 925°, 0.006 sec. residence time, using the procedure described for *p*-xylene[12] and 1,2-di-*o*-tolylethane (m.p. 50–55°; τ-values 2.99 for phenyl, 7.24 for methylene and 7.77 for methyl) was obtained in 4% yield per pass. The compound was purified further by sublimation and subsequent recrystallization from methyl alcohol to yield white needle-like crystals (m.p. 63–65°).

(b) *o*-Xylene was pyrolyzed at 1000° and 0.023 sec. residence time and anthracene was obtained in 13% yield per pass. The product was purified by sublimation and recrystallization from methanol to afford anthracene in the form of white platelets (m.p. 210–212°).

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Contribution to the Structure of the Ferrichrome Compounds: Characterization of the Acyl Moieties of the Hydroxamate Functions[1,2]

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The acyl moieties of the hydroxamate functions of ferrichrome and ferrichrome A have been characterized as three residues each of acetic and *trans*-β-methylglutaconic acid, respectively.

The isolation and general properties of the ferrichrome compounds have been reviewed elsewhere.[3a] These substances and other possibly related products appear to be widely distributed in microbial species. They are characterized chemically by their ability to form stable coördination compounds with ferric ion; biologically some of them, *e.g.*, ferrichrome itself, are distinguished by their potent growth-promoting activity for a number of unicellular organisms. Their widespread distribution and potent physiological activity appeared to justify structural work on these products in spite of the fact that the pure compounds can only be obtained on a milligram scale. Since all of the compounds which exhibit very intense growth-factor activity either contain iron or are capable of complexing this element,[3] it was concluded that the iron-binding center might also be the seat of biological activity. Consequently, it was decided to concentrate our efforts on this part of the molecule.

Ferrichrome is a neutral substance and ferrichrome A contains three carboxyl groups per mole.[3] When the iron was removed from either of these compounds, electrometric titration of the product revealed the presence of three new ionizable groups with average pK_a' of about 9. Concomitant measurements of light absorption in the ultraviolet (250 mμ) showed this pK to be spectrophotometrically operable. Thus, in alkali the ultraviolet absorption was intensified and shifted to the red in a manner somewhat characteristic of keto-enol tautomerism. It was speculated[3] that enolic groupings might be wholly or partly responsible for binding the iron atom, although the intensity of the ultraviolet absorption in alkali was much less than what would be expected for the usual enol.

The problem remained at this level of development until an unknown spot on a paper chromatogram, prepared from an acid hydrolysate of ferrichrome, was identified as hydroxylamine.[3b] A progress curve for the liberation of hydroxylamine showed that the latter was bound too firmly to be present as an oxime. This experiment served to focus attention on the hydroxamic acid grouping as a possible source of NH_2OH in the ferrichrome compounds. That these natural products are indeed ferric hydroxamates is evident from these facts:

1. Prolonged acid hydrolysis of ferrichrome or ferrichrome A liberates 3 moles of "hydroxylamine."

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(3) (a) J. B. Neilands, *Bact. Rev.*, **21**, 101 (1957). (b) The authors are indebted to Mr. B. Burnham for assistance with this phase of the investigation.