tical to those of authentic 1,1-dibenzylethane. The absence of 1,4-diphenylbutane in these products was easily shown since its emergence time from a g.l.c. column was greatly different from that of 1,1-dibenzylethane described previously.

Kharasch Reaction on 1,1-Dibenzyl-2-chloroethane.—To a blue-green solution made from 2.4 g. (10 mmoles) of 1,1-dibenzyl-2-chloroethane, 0.05 g. of cobaltous bromide and 20 ml. of anhydrous ether, was slowly (1 hr.) added, with stirring at room temperature, 15 mmoles of ethylmagnesium bromide in 25 ml. of ether. Further portions of cobaltous bromide (total, 0.2 g.) were added during the Grignard addition. The solution was refluxed for 30 min., cooled, hydrolyzed, and the ether solution dried over anhydrous potassium carbonate after washing with water. The solution was concentrated, dissolved in benzene, and hydrogenated as in the previous manner to saturate olefins which may have been formed by disproportionation reactions. From the amount of hydrogen consumed, the material was estimated to contain 20–30% monoolefin. Analyses of the final solution by g.l.c. indicated a yield of ~70% 1,1-dibenzylethane. A compound having the same retention time as authenic 1,4-diphenylbutane accounted for $\leqq 0.5\%$ of the $C_{16}H_{18}$ material recovered. Approximately 10% of the starting chloride was recovered as shown by g.l.c.

3-Phenylpropanoic-1-C^{14} Acid.—In a suitable flask were placed 100 g. (0.712 mole) of 2-phenyl-1-chloroethane 46.6 g. (0.950 mole) of sodium cyanide, 0.05 mc. of $KC^{14}N$, 100 ml. of ethanol, and 55 ml. of water. After refluxing 38 hr., 400 ml. of benzene and 400 ml. of water were added and the layers separated. The water layer was extracted with additional benzene and the total benzene extracts combined. The latter was washed with water and dried over calcium chloride. The benzene was removed by distillation and the crude 3-phenylpropanenitrile-1-C^{14} refluxed with a solution of 125 ml. of concentrated sulfuric acid, 125 ml. of glacial acetic acid, and 125 ml. of water for 2.5 hr. The mixture was cooled and poured into 250 ml. of ice–water. The oily layer was diluted with ether and the 3-phenylpropanoic-1-C^{14} acid extracted from the ether with dilute sodium hydroxide solution. The acid was recovered by precipitation with dilute hydrochloric acid.

3-Phenyl-1-chloropropane-1-C^{14}.—The 3-phenylpropanoic-1-C^{14} acid was converted to the chloride in a manner similar to that used in the preparation of 1,1-dibenzyl-2-chloroethane. After distillation, 3-phenyl-1-chloropropane-1-C^{14}, b.p. 89.6–90.0° (9.5 mm.), was obtained in an over-all yield, based on 2-phenyl-1-chloroethane, of 21.4%.

4-Phenylbutanal-2-C^{14}.—This aldehyde was prepared in a manner similar to that used by Cohen[24] for the preparation of 3-phenylpropanal. The Grignard reagent prepared from 1.0 mole of 3-phenyl-1-chloropropane-1-C^{14} was converted to the acetal by treatment with triethyl orthoformate. After hydrolysis, the aldehyde was recovered as the bisulfite adduct. The 4-phenylbutanal-2-C^{14}, obtained by steam distillation of a sodium carbonate solution of the bisulfite adduct, was further purified by distillation, b.p. ~159° (10 mm.), to give a 21.3% yield. A 2,4-dinitrophenylhydrazone derivative of the aldehyde was made, m.p. 111.5–112.5°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.52; H, 4.91; N, 17.07. Found: C, 59.0; H, 4.9; N, 16.9.

A small sample of this aldehyde was oxidized *via* a basic potassium permanganate solution to benzoic acid in 32.5% yield. After recrystallization from *n*-pentane–methylene chloride, the acid, m.p. 120–120.5°, was shown to be devoid of any C^{14}; thereby demonstrating that rearrangement had not occurred during the synthesis.

Decarbonylation of 4-Phenylbutanal-2-C^{14}.—Approximately 54 mmoles of the aldehyde in 50 ml. of *o*-dichlorobenzene containing 18 mmoles of di-*t*-butyl peroxide was decarbonylated at 149°. After gas evolution was completed, 35 mmoles of carbon monoxide (64.3%) was recovered. The *n*-propylbenzene-C^{14}, resulting from the decarbonylation, was diluted with 20 g. of *n*-propylbenzene and separated from the *o*-dichlorobenzene solution by distillation to give 16.7 g., b.p. 159.1–159.3°. The *n*-propylbenzene was shown to be 99.2% pure by g.l.c. analysis.

The degree of rearrangement from this reaction was found by determining the relative amounts of 3-phenylpropane-1-C^{14} and 1-phenylpropane-1-C^{14} in the product. This was accomplished by comparing the total C^{14} activity of the *n*-propylbenzene-C^{14} and that of its oxidation product, benzoic acid.

C^{14}-activities measured: product *n*-propylbenzene-C^{14}, 1,274 d.p.m./mmole; benzoic acid from oxidation of the *n*-propylbenzene-C^{14}, $\leqq 2$ d.p.m./mmole. Therefore, the extent of rearrangement was $\leqq 0.16\%$.

Kharasch Reaction of 3-Phenyl-1-chloropropane-1-C^{14}.—The reaction of this chloride was carried out in a manner similar to that for 1,1-dibenzyl-2-chloroethane, using 17.5 g. (0.113 mole) of 3-phenyl-1-chloropropane-1-C^{14}, a total of 1.4 g. (0.01 mole) of cobaltous bromide, and 0.15 mole of ethylmagnesium bromide. After refluxing for 2 hr., 20 ml. of *n*-propylbenzene was added to dilute the *n*-propylbenzene-C^{14} product. The yield of β-methylstyrene and *n*-propylbenzene was estimated to be 23%. The amount of rearrangement was determined as previously mentioned for the decarbonylation reaction.

C^{14}-Activities measured: product *n*-propylbenzene-C^{14}, 1,760 d.p.m./mmole; benzoic acid, ~0 d.p.m./mmole. No detectable rearrangement occurred during the reaction.

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[24] H. Cohen, *J. Chem. Soc.*, 432 (1935).

The Chemistry of Xylylenes. XX. The Gas Phase Oxidation of *p*-Methylbenzyl Radicals and *p*-Xylene

L. A. ERREDE AND W. D. ENGLISH

Contribution No. 236 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota[1]

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p-Methylbenzyl radicals generated *via* fast flow pyrolysis of *p*-xylene are converted to *p*-xylylene as the gas stream travels away from the furnace. The *p*-methylbenzyl radicals and *p*-xylylene produced in this way are oxidized to *p*-toluic acid and terephthalic acid, respectively, when the hydrocarbon stream is quenched with pyrolyzed nitric acid or nitrogen dioxide. *p*-Toluic acid is isolated exclusively when the two streams are mixed at or near the pyrolysis zone, whereas terephthalic acid is isolated exclusively when the two streams are mixed at a considerable distance away from the pyrolysis zone. Aldehydes are obtained instead of acids when the hydrocarbon stream is mixed with a limited amount of pyrolyzed nitric acid. The yield of oxidized products is about equal to the per cent conversion of *p*-xylene to *p*-methylbenzyl radicals in the pyrolysis zone of the reactor. In contrast, only nitroxylene, dinitroxylenes, and *p*-methylbenzyl nitrate are obtained when pyrolyzed *p*-xylene is quenched with nonpyrolyzed nitric acid.

It was reported in a previous publication[2] that the mechanism for formation of *p*-xylylene *via* fast flow pyrolysis of *p*-xylene at low pressure involves thermal rupture of the C—H bond to give hydrogen and *p*-methylbenzyl radicals[3] (equations 1 and 2), and subse-

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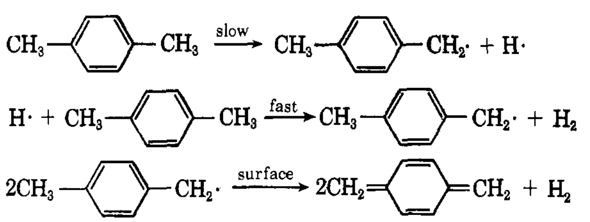
[1] This work was done in the laboratories of the M. W. Kellogg Company. The data were acquired by the Minnesota Mining and Mfg. Company with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Company in March, 1957.

[2] L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 73 (1963).

[3] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).



(1)

(2)

(3)

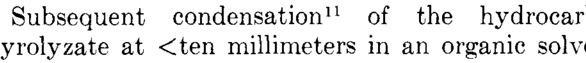
quent catalytic dehydrogenation of these monoradicals to *p*-xylylene as the pyrolysate travels away from the furnace[2] (equation 3).

It was demonstrated[2,4] that *p*-methylbenzyl radicals and *p*-xylylene could be trapped in gas phase by quenching this hydrocarbon pyrolysate with a second stream of radicals. The products isolated were those formed *via* random coupling of the radical species present at the point of mixing. Monofunctional derivatives were obtained when the two streams were allowed to mix at a point just beyond the pyrolysis zone; whereas difunctional derivatives were obtained when the point of mixing was located far downstream. Thus, *p*-methylbenzyl chloride, β,β-dichloro-*p*-methylstyrene, α,α'-dichloro-*p*-xylene, and α,α'-bistrichloromethyl-*p*-xylene were some of the compounds produced by mixing with chlorocarbon radical streams[4-6] at the appropriate quench point.

This technique appeared to be applicable to gas phase oxidation of mono- and diradicals and our research efforts were directed accordingly.

Results and Discussion

The most obvious oxidizing agent for gas phase oxidation of radicals is oxygen. Surprisingly, only a trace amount of toluic or terephthalic acid was obtained when *p*-xylene and oxygen were subjected to fast flow copyrolysis at low pressure (less than ten millimeters). Even when the *p*-xylene to oxygen ratio was 3 to 1, the major products isolated were those normally produced *via* fast flow pyrolysis of *p*-xylene.[7-10] Moreover, the oxygen present did not interfere with the catalytic conversion of *p*-methylbenzyl radicals to *p*-xylylene. In each case, the conversion of *p*-xylene to *p*-methylbenzyl radicals, isolated as various hydrocarbon products,[10] was within experimental error of that amount anticipated when *p*-xylene alone is subjected to fast flow pyrolysis[10] at the same temperature and residence time. Apparently the formation of benzyl peroxy radicals is a reversible reaction as indicated by equation 4, and the equilibrium is far to the left at very low pressure.



(4)

Subsequent condensation[11] of the hydrocarbon pyrolyzate at $<$ten millimeters in an organic solvent[7] kept at -78° affords an oxygen-free solution containing *p*-xylylene. Polymerization to oxygen free poly(*p*-xylylene) occurs when the solution is warmed to room temperature.[7,12]

In an independent experiment performed elsewhere by M. Szwarc,[13] oxygen was recovered quantitatively after the low pressure oxygen–*p*-xylene gas mixture was subjected to fast flow pyrolysis at 1000°.

That the formation of alkyl peroxy radicals can be a reversible reaction was also observed by Matsugashita and Shinohara.[14] These workers reported that addition of oxygen to polymeric perfluorocarbon radicals gives the corresponding polymeric perfluorocarbon peroxy radicals. The original radical species are obtained, however, when the partial pressure of oxygen in contact with the polymer is markedly decreased.

In contrast to the results obtained with molecular oxygen, gas phase oxidation of the *p*-methylbenzyl radicals and *p*-xylylene molecules occurred readily when the hydrocarbon pyrolyzate was mixed at a predetermined point downstream with pyrolyzed nitric acid. The two streams were pyrolyzed in separate but concentric tubes. *p*-Xylene flowed through the outer tube while nitric acid was metered through the inner one. Only monofunctional oxidation products of *p*-xylene were isolated when the two streams were allowed to blend within the pyrolysis zone where the hydrocarbon stream contains *p*-methylbenzyl radicals free of *p*-xylylene. On the other hand, difunctional oxidation products were isolated exclusively when the two streams were allowed to blend in the postpyrolysis zone after the *p*-methylbenzyl radicals in the hydrocarbon stream were converted to *p*-xylylene. A mixture of mono- and difunctional oxidation products were obtained when the hydrocarbon stream was quenched at an intermediate point. Aromatic aldehydes were obtained as the major product when the pyrolysis was carried out using a limited amount of nitric acid. The conversion of *p*-xylene to products of oxidation per pass was equal to that amount of *p*-methylbenzyl radicals generated when *p*-xylene is pyrolyzed at the same temperature and residence time.[10]

In order to demonstrate that the formation of carboxylic acids was the result of gas phase oxidation of *p*-methylbenzyl radicals and/or *p*-xylylene by the thermal degradation products of nitric acid,[15] a stream of pyrolyzed *p*-xylene was quenched with a gas stream of nonpyrolyzed nitric acid at a point six inches beyond the pyrolysis zone. The pyrolysate was collected in a solvent kept at -78° and separated thereafter as described in the Experimental. Only trace amounts of aromatic carboxylic acids were isolated. The major products were mono- and dinitroxylenes (4% and 30% yields, respectively, based on *p*-xylene). Apparently the dinitroxylenes were formed *via* gas phase nitration. A small amount of *p*-methylbenzyl nitrate was also isolated. This compound could have formed *via* addition of nitric acid to *p*-xylylene since it is

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[4] L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 69 (1963).

[5] L. A. Errede and J. P. Cassidy, *ibid*, **67**, 1358 (1963).

[6] L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, **28**, 1059 (1963).

[7] L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).

[8] L. A. Errede and J. P. Cassidy, *ibid.*, **82**, 3653 (1960).

[9] L. A. Errede, R. S. Gregorian and J. M. Hoyt, *ibid.*, **82**, 5218 (1960).

[10] L. A. Errede and F. DeMaria, *J. Phys. Chem.*, **66**, 2664 (1962).

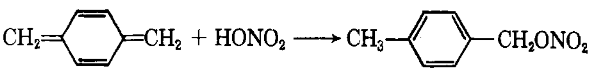
[11] Oxygen does not condense at this temperature and pressure.

[12] L. A. Errede and S. L. Hopwood, Jr., *J. Am. Chem. Soc.*, **79**, 6507 (1957).

[13] M. Szwarc, private communication.

[14] T. Matsugashita and K. Shinohara, *J. Chem. Phys.*, **35**, 1652 (1961).

[15] Nitrogen dioxide is a major product of thermal degradation of nitric acid as indicated by evolution of large volumes of nitrogen dioxide when the cold solution of reaction products was warmed from -78° to room temperature. Nitric oxide was also produced as indicated by the blue-green color in the liquid nitrogen cold trap.

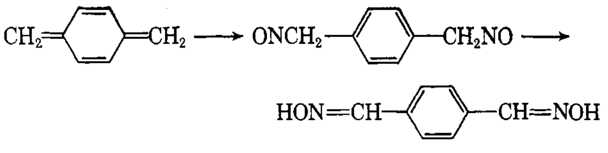


known that *p*-xylylene reacts readily with acids to afford the corresponding *p*-methylbenzyl esters.[16]

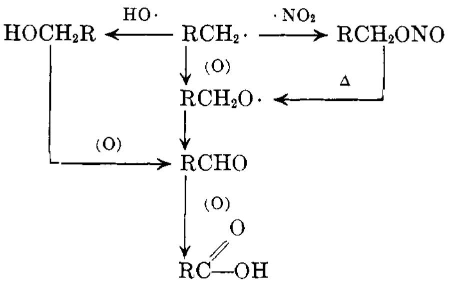
When pyrolyzed *p*-xylene was collected in a cold (−78°) slurry of nitric acid in toluene, the major product was mononitroxylene. Nitrated poly(*p*-xylylene) and related products were also isolated in amounts that were consistent with the anticipated amount of *p*-methylbenzyl radicals produced in the pyrolysis zone as a function of temperature and residence time.[10] No carboxylic acids and only a relatively small amount of nitrated products were obtained when pyrolyzed nitric acid was quenched downstream with nonpyrolyzed *p*-xylene.

Nitrogen dioxide can be used instead of pyrolyzed nitric acid for oxidation of *p*-methylbenzyl radicals and *p*-xylylene to the corresponding acid. Thus, nitrogen dioxide and *p*-xylene were pyrolyzed in concentric tubes, and the pyrolysates were allowed to blend downstream at a point where the ratio of *p*-methylbenzyl radicals to *p*-xylylene in the hydrocarbon stream[2] was about 7:4. About 70% of the *p*-methylbenzyl radicals produced in the pyrolysis zone was isolated as *p*-toluic and terephthalic acids in the ratio of about 2:1. If a stream of pyrolyzed *p*-xylene is quenched with nonpyrolyzed nitrogen dioxide, a mixture of acidic low molecular weight aromatic compounds containing nitrogen bonded to the terminal methylene groups is obtained. Although of lower molecular weight, the mixture is similar to that reported earlier[17] for reaction of *p*-xylylene with nitrogen dioxide in solution.

It was reported[17] that a mixture of low molecular weight telomeric dialdoximes is obtained when a *p*-xylylene solution saturated with nitric oxide at −78° is warmed to room temperature. Only a small amount of terephthaldoxime is formed in this way since the solubility of nitric oxide in organic solvents is very low even at −78°. The selectivity for terephthaldoxime formation is markedly improved, however, if the *p*-xylene pyrolysate is blended in the gas phase with an excess of nitric oxide at a point where the temperature is not above 200°, and the resulting gas stream then collected in the cold solvent. Blending the two gas streams at high temperatures leads to thermal degradation of the nitroso product.



These results show that the carboxylic acids were produced by oxidation of the hydrocarbon radicals and not by oxidation of *p*-xylene. They also show that the oxidizing agents are the thermal degradation products of nitric acid, such as HO·, nitrogen dioxide, and atomic oxygen, and not nitric acid. The oxidation products probably are formed by stepwise reactions involving random radical coupling, degradation, and continued oxidation as indicated above.



Experimental

Co-Pyrolysis of *p*-Xylene and Nitric Acid.—The pyrolysis system shown in Fig. 1 of ref. 7 was modified to include a second vaporizer for metering aqueous nitric acid (68%). The system was evacuated to 6 mm., and *p*-xylene (3.17 moles) and nitric acid (1.05 moles) were metered to the system at the rate of 0.045 and 0.015 moles/min., respectively. The two gas streams were mixed before they entered the furnace where fast flow pyrolysis occurred at 1030°. The pyrolysate was collected in 4 l. of hexane kept at −78°. The cold trap was warmed to room temperature to afford a three-phase mixture of hexane solution, aqueous acid solution (43 g.), and a black tar (9 g.). Large volumes of nitrogen dioxide were given off when the mixture was warmed to room temperature. The last traces were removed by a current of nitrogen. The hexane solution was washed with water and the solvent was removed by rapid evaporation at 100° and 60 mm. The yellow liquid residue (154 g.) was a mixture of aldehydes and aromatic hydrocarbons having no NO_2 groups as indicated by infrared analysis and negative qualitative test for NO_2 using ferrous ammonium sulfate in alcoholic potassium hydroxide. The mixture was separated by distillation at atmospheric pressure to give three main fractions. Fraction 1 (76 g., b.p. 137–141°) was identified by infrared analysis as *p*-xylene. Fraction 2 (32 g., b.p. 196–202°, $n^{14}\text{D}$ 1.5433) was identified as *p*-tolualdehyde (lit.[18] b.p. 204–205°, $n^{14}\text{D}$ 1.5483[19]) by infrared analysis and by converting a sample to its 2,4-dinitrophenylhydrazone derivative (m.p. 229–230°, no depression with authentic sample) in good yield. Fraction 3 (35 g. of residue) was separated further by distillation at 2 mm. to give three additional major fractions. (a) Infrared analysis indicated that this (2.2 g., b.p. 64–80°) was mostly *p*-tolualdehyde with some 1,2-di-*p*-tolylethane and diarylmethanes present as impurities. (b) Infrared analysis indicated that this (18.7 g., b.p. 125–137°) was a mixture of 1,2-di-*p*-tolylethane, diarylmethanes, and a small amount of acid material. The mixture was extracted with dilute sodium hydroxide and the residue was dissolved in methanol. The methanol solution was chilled to −78° to precipitate 1,2-di-*p*-tolylethane (4.5 g.) in the form of pearl white platelets (m.p. 74–75°, no depression with authentic sample). The methanol solution was evaporated to dryness leaving a residue (10 g.) which was a mixture of alkylated diphenylmethanes and 1,2-di-*p*-tolylethane as indicated by infrared analysis. (c) Infrared analysis indicated that this (9 g. residue, b.p. >150°) was a complex mixture of aromatic hydrocarbons and some acidic material. The residue was leached with dilute sodium hydroxide. The alkaline extract was combined with corresponding extract from fraction b and the resulting solution was acidified with hydrochloric acid to liberate the organic acid (3 g.) which was removed by filtration. The acid was recrystallized from hot water to yield *p*-toluic acid in the form of fine white needles (m.p. 174–175°, no depression with authentic sample). The compound was also identified by its infrared spectrum.

Thus, 3.2 moles of *p*-xylene and 1.05 moles of nitric acid were co-pyrolyzed to afford 0.28 mole of *p*-tolualdehyde, 0.02 mole of *p*-toluic acid, and 0.24 mole of *p*-methylbenzyl radical equivalents isolated as the products 1,2-di-*p*-tolylethane and diarylmethane.[8]

Co-Axial Pyrolysis of *p*-Xylylene and Nitric Acid.—The internal thermowell no. 17 of the pyrolysis system shown in Fig. 1 of ref. 7 was replaced by an open end quartz tube through which nitric

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[16] L. A. Errede, J. M. Hoyt, and R. S. Gregorian, *J. Am. Chem. Soc.*, **82**, 5224 (1960).

[17] L. A. Errede and J. M. Hoyt, *ibid.*, **82**, 436 (1960).

[18] E. Borneman, *Ber.*, **17**, 1462 (1884).

[19] V. Hanzlick and A. Bianchi, *ibid.*, **32**, 1285 (1899).

acid could be metered to the pyrolysis system. This tube extended to a point 3 in. beyond the furnace so that blending of the pyrolyzed nitric acid stream and the pyrolyzed *p*-xylene stream would occur at a point 6.5 in. away from the pyrolysis zone.[2] The space in the outer concentric tube between the pyrolysis zone and the blend point was filled with five quartz tubes (6 in. long, 6-mm. o.d., 4-mm. i.d.) to ensure complete conversion of *p*-methylbenzyl radicals to *p*-xylylene in the *p*-xylene pyrolysate before the hydrocarbon stream reached the blend point.[2] The temperature was recorded by means of a sliding thermocouple placed between the furnace and the outer pyrolysis tube. The system was evacuated to 4 mm., and *p*-xylene (1.98 moles) and nitric acid (3.4 moles) were metered separately to the system through the concentric tubes at the rate of 0.016 and 0.027 moles/mm., respectively. Pyrolysis of *p*-xylene occurred at 930° for 0.01 sec. (conditions which are known to give about 0.24 mole of *p*-methylbenzyl radicals[10]). The pyrolysate mixture was collected in hexane (4 l.) kept at −78°. The resulting mixture was warmed to room temperature with evolution of much nitrogen dioxide. The last traces were removed by a stream of nitrogen. A three-phase system was obtained and this was separated into its aqueous acid, organic liquid, and organic solid components. The solid (27 g.) was dissolved in aqueous sodium carbonate. The organic phase was extracted with aqueous sodium carbonate. The two alkali carbonate solutions were combined and then acidified with aqueous hydrochloric acid. The organic acid liberated (26 g., 0.16 mole) was collected by filtration. The acid was leached with methanol but none dissolved indicating the absence of *p*-toluic acid. The acid did not melt below 300°. Its infrared spectrum was virtually identical with that of terephthalic acid. A small sample was converted to its dimethyl ester by treatment with fused phosphorus pentachloride and subsequent addition to methanol. The melting point of the dimethyl terephthalate (m.p. 138–139°) produced in this way showed no depression when mixed with an authentic sample. The hexane solution was evaporated to dryness and a mixture of the usual aromatic hydrocarbons[8] was obtained as residue (9 g.).

Thus, pyrolysis of *p*-xylene (1.98 moles) was carried out in such a way as to afford about 0.24 mole of *p*-methylbenzyl radicals and about 70% of these were isolated as terephthalic acid and about 30% as a mixture of aromatic hydrocarbons (1,2-di-*p*-tolylethane, methylated diphenylmethanes, and anthracenes).

Co-Axial Pyrolysis of *p*-Xylene and Nitrogen Dioxide.—The internal thermowell no. 17 of the pyrolysis system shown in Fig. 1 of ref. 7 was replaced by an open end tube through which nitrogen dioxide was led into the system, which was evacuated to 5 mm. *p*-Xylene (7.3 moles through the outer tube) and nitrogen dioxide (25.6 moles through the inner tube) were metered to the system at the rate of 0.0545 and 0.175 mole/min., respectively. Pyrolysis of *p*-xylene occurred at 1000° for 0.002 sec. and the two pyrolyzate streams were allowed to blend at a point 6.5 in. away from the end of the mutual pyrolysis zone. Previous experiments had shown that the pyrolysis conditions used in this experiment afford about 0.18 mole of *p*-methylbenzyl radicals[10] and that about 40% of these are converted to *p*-xylylene by the time the hydrocarbon stream reaches the blend point[2] where the temperature is about 450°. The pyrolysate mixture was collected in hexane kept at −78°. When the resulting solution was warmed to room temperature, the usual three-phase mixture was obtained. The solid (9 g.) was removed by filtration, dissolved in aqueous sodium carbonate, and reprecipitated by addition of hydrochloric acid. This product was identified as terephthalic acid by its infrared spectrum. The organic layer was extracted with aqueous sodium carbonate. Acidification of the extract with dilute hydrochloric acid gave 11 g. of impure *p*-toluic acid (165–170°). The organic layer was evaporated to dryness and a mixture of aromatic hydrocarbons (1,2-di-*p*-tolylethane and diaryl methanes) was obtained as residue (6 g.).

Reaction of Pyrolyzed *p*-Xylene with Nonpyrolyzed Nitric Acid.—*p*-Xylene (1.8 moles) was metered at the rate of 0.025 mole/min. to the pyrolysis system evacuated to 2 mm. Pyrolysis occurred at 1030° for an average residence time of 0.006 sec. These conditions are known to produce about 0.2 mole of *p*-methylbenzyl radicals.[10] At a point 6.5 in. downstream from the pyrolysis zone, the pyrolysate was mixed with nonpyrolyzed 90% nitric acid (10 moles), metered countercurrent to the system at the rate of 0.142 mole/min. The temperature at the blend point was about 450°. The gas mixture was collected about 3 ft. from the blend point in hexane (4 l.) kept at −78°. The absence of nitric oxide and nitrogen dioxide in the liquid nitrogen and Dry Ice traps, respectively, indicated that little or no thermal degradation of nitric acid had occurred.

The resulting pyrolysate solution was warmed to room temperature. About 1 g. of poly(*p*-xylylene) was isolated as film that adhered to the walls of the receiver about the level of the liquid. The aqueous and organic phases were separated by means of a separatory funnel.

The organic layer was extracted with dilute aqueous sodium hydroxide, but no organic acid was liberated when the alkaline solution was acidified with hydrochloric acid. The hexane in the organic phase was removed by distillation at atmospheric pressure. The residue (26 g.) was separated by distillation at 8 mm. to give two fractions. (1) The infrared spectrum of this fraction (11 g., b.p. 103–104°) was similar to that of nitro-*p*-xylene. The index of refraction ($n^{27}\text{D}$ 1.536) and density (d^{27} 1.149) of the light yellow oil was in agreement with the corresponding data measured on an authentic sample ($n^{27}\text{D}$ 1.539, d^{27} 1.148). A small sample of this oil (1.5 g.) was oxidized by potassium dichromate (11 g.) in sulfuric acid and water to 3-nitro-*p*-toluic acid (m.p. 186–187°) (no depression with authentic sample). (2) The infrared spectrum of this 15-g. residue indicated that this was a mixture of nitro-aromatic compounds.

The aqueous nitric acid phase was diluted with water and a copious precipitate formed immediately. The product (95 g.) was a mixture of nitroxylenes as indicated by infrared analysis. Repeated fractional crystallization from toluene and methanol gave three major fractions classified according to melting point. (1) Yield, 2.4 g., m.p. 97–98°. The elementary analysis (C, 49.3; H, 4.7; N, 13.4) corresponded to the empirical formula for dinitroxylenes, $C_8H_8N_2O_4$ (C, 49.0; H, 4.1). The infrared spectrum, however, indicated that this was a mixture of nitroxylenes, probably the 2,3- and the 2,6-di-nitro-*p*-xylylene since these are known to form a 1:1 adduct that melts at 99°.[20] (2) Yield, 40 g., m.p. 95–102°. The infrared spectrum was similar to fraction 1 and indicated a mixture of nitroxylylenes. (3) Yield, 51 g., m.p. 79–88°. This too was a mixture of nitroxylenes as indicated by infrared analysis. Fractions 2 and 3 and the nitroxylenes residue from the organic layer were reconstituted and an attempt was made to separate the product by liquid chromatography. The results were no better than those realized *via* fractional recrystallization. A small sample (1 g.), m.p. 92–93°, was isolated, however, which could be the 2,3-dinitro-*p*-xylene (lit.[21] m.p. 93°).

In summary, 1.8 moles of *p*-xylene was pyrolyzed and the pyrolyzate was quenched with 10 moles of nonpyrolyzed nitric acid to give about 0.55 mole of dinitro-*p*-xylene (30% yield) and about 0.07 mole of nitro-*p*-xylene (4% yield). No organic acid or aldehydes were isolated despite the formation of about 0.2 mole of *p*-methylbenzyl radicals before quenching with nitric acid.

In another experiment, *p*-xylene (1.88 moles) was pyrolyzed at 1000° and 4 mm. for 0.008-sec. residence time. The pyrolyzate was collected in a slurry of solid nitric acid (8.5 moles) in toluene (4 l.) kept at −78°. The reaction mixture was warmed to room temperature and separated as described previously. Again, no organic acid was isolated. Instead, 22% of the *p*-xylene metered to the system was isolated as nitro-*p*-xylene, 2% as dinitro-*p*-xylene, 6% as nitrated poly(*p*-xylylene) containing 7.4%; N, and 1% as *p*-methylbenzyl nitrate [b.p. 110–111° (10 mm.); $n^{25.5}\text{D}$ 1.5174; $d^{25.5}$, 1.153].

Anal. Calcd. for $C_8H_9NO_3$: C, 57.49; H, 5.42; MRD 43.57. Found: C, 57.7; H, 5.35; MRD 43.7.

An authentic sample of *p*-methylbenzyl nitrate was prepared by reaction of pulverized silver nitrate with *p*-methylbenzyl chloride in ether. The physical constants were in good agreement with those reported here, and the infrared spectra of the two samples were virtually identical.

Reaction of Pyrolyzed Nitric Acid with Nonpyrolyzed *p*-Xylene.—Nitric acid (3.4 moles) metered to the system at the rate of 0.041 mole/min. was pyrolyzed at 1030° and 2 mm. for an average 0.004-sec. residence time and the pyrolysate was mixed with nonpyrolyzed *p*-xylene (3.0 moles) at a point 6 in. downstream from the pyrolysis zone. The gas stream was condensed in hexane (4 l.) kept at −78°. The mixture was warmed to room temperature and separated as described previously. Almost all of the *p*-xylene was recovered unchanged and only 0.9 g. of nitrated product was isolated as an oil (b.p. > 140°). This oil was insoluble in dilute aqueous sodium hydroxide.

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(20) P. Yannasch and C. Stunkel, *Ber.*, **14**, 1146 (1881).

(21) Lange's "Handbook of Organic Chemistry."