For 1,2,4,5-tetraethylbenzene:

$$\log p = 54.6612 - 5905.5/T - 14.8886 \log T$$

For 1,2,3,5-tetraethylbenzene:

$$\log p = 18.1202 - 3756/T - 2.9332 \log T$$

For 1,2,3,4-tetraethylbenzene:

$$\log p = 17.4635 - 3637/T - 2.8165 \log T$$

These equations, however, are only approximate, the average deviations of the first being ±2 mm., of the second, omitting the two largest values which were much too large, ±2.5 mm. and of the third ±6 mm.

TABLE I

PHYSICAL PROPERTIES OF THE TETRAETHYLBENZENES

	Symmetrical	Unsymmetrical	Vicinal
B. p., °C.	246.8 (734 mm.)[a] 250[c] 248 (755 mm.)[b]	247.4 (734 mm.)[a]	251.1 (734 mm.)[a] 254[c]
F. p., °C.	+10[a] +13[c]	−21[a]	Does not freeze[a] at −50
$n^{20}D$	1.5054[a] 1.5041 (16°)[b]	1.5056[a]	1.5125[a] 1.50845[d]
d^{20}	0.8788[a] .8884 (16°)[b]	0.8799[a]	0.8875[a] .88664 (19.6°)[d]

[a] New results reported in the present study. [b] Klages and Keil, *Ber.*, **36**, 1632 (1903). [c] Jacobsen, *ibid.*, **21**, 2814, 2819 (1888). [d] Perkin, *J. Chem. Soc.*, **77**, 280 (1900).

TABLE II

VAPOR PRESSURES OF THE TETRAETHYLBENZENES

Symmetrical		Unsymmetrical		Vicinal	
Press., mm.	B. p., °C.	Press., mm.	B. p., °C.	Press., mm.	B. p., °C.
3	97.6	3	96.6	2	95.2
4	102.6	4	104.0	4	107.0
10.5	128.4	15	134.4	10	129.4
22.5	141.4	32.5	148.5	11.5	132.4
57	159.2	58	160.3	30.5	151.0
123	180.6	129.5	182.6	51	164.1
240	202.6	246	204.1	124	185.2
546	233.8	530	232.8	224.5	204.1
734	246.8	734	247.4	578.5	241.8
				734	251.1

Summary

1. The following physical properties of highly purified tetraethylbenzenes have been determined: refractive indices, densities, freezing points, vapor pressures.

2. The freezing point diagram of mixtures of 1,2,4,5- and 1,2,3,5-tetraethylbenzenes has been constructed.

3. *sym*- and *unsym*-tetraethylbenzenes have practically identical refractive indices and vapor pressures throughout the entire range studied.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 2, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Jacobsen Reaction. VII.[1] Polyethylbenzenes

BY LEE IRVIN SMITH AND CYRUS O. GUSS[2]

In the previous paper[1b] the results of a study of the Jacobsen rearrangements of some ethyltrimethylbenzenes, namely, 5-ethylpseudocumene, 3-ethylpseudocumene and ethylmesitylene, were reported. The second of these hydrocarbons did not undergo any rearrangement in contact with sulfuric acid, but the other two were rearranged into 3-ethylpseudocumene (25–35%), prehnitene (10%), an ethyl-*m*-xylene (12%) and a trimethylbenzene (5%). In these rearrangements, the ethyl group migrated more readily than one of the methyl groups, but the reaction was accompanied by three types of cleavage: loss of the ethyl group, loss of a methyl group, and cleavage of the ethyl group to a methyl group. Moreover, there was a great difference between ethylmesitylene and 5-ethylpseudocumene in the ease with which the rearrangement occurred; at 60–70°, the former required six hours for complete change, while one hour sufficed for the latter.

To obtain more information concerning the Jacobsen rearrangement of ethylated benzenes, six polyethylbenzenes, 1,2,4- and 1,3,5-triethylbenzenes, the three tetraethylbenzenes, and pentaethylbenzene, have been studied. Very few reports are to be found in the literature dealing with rearrangements of polyethylbenzenes. Jacobsen[3] dissolved pentaethylbenzene in fuming sulfuric acid; after the solution stood for several days, he noted the formation of hexa-ethylbenzene and found that the solution contained a sulfonic acid whose amide melted at 107°, and he identified this as derived from 1,2,3,4-tetraethylbenzene. Jacobsen also stated that when pentaethylbenzene was heated with sulfuric acid, neither hexa-

(1) (a) Polyalkylbenzenes XXIX. Paper XXVIII, THIS JOURNAL, **62**, 2630 (1940); (b) Paper VI on the Jacobsen Reaction, THIS JOURNAL, **61**, 989 (1939).

(2) Abstracted from a thesis by Cyrus O. Guss, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) Jacobsen, *Ber.*, **21**, 2814, 2819 (1888).

ethylbenzene nor a tetraethylbenzene sulfonic acid could be isolated from the product. Galle[4] also carried out this reaction, with essentially the same results, and in an attempt to separate into its constituents a tetraethylbenzene fraction, he shook the oil with sulfuric acid. The resulting product was 1,2,3,4-tetraethylbenzene sulfonic acid, and Galle therefore stated that the corresponding hydrocarbon was formed when benzene was ethylated. Jacobsen, realizing that a rearrangement might have occurred during Galle's experiment, repeated the sulfonation but used chlorosulfonic acid and separated the sulfonic acids as salts from the mixture. He isolated two sulfonic acids, and obtained evidence for a third, from which he concluded that ethylation of benzene produced all of the tetraethylbenzenes. In view of the evidence presented below, it must be concluded that both Galle and Jacobsen, unaware of the extreme ease with which the tetraethylbenzenes rearrange, were reporting upon the constituents of mixtures which had been wholly or in part rearranged by contact with sulfuric acid and which therefore did not represent the true composition of the original tetraethyl fractions obtained by them.

The two triethylbenzenes, 1,2,4- and 1,3,5-, isolated from the triethylbenzene fraction by the method of Dillingham and Reid[5] were merely sulfonated by heating them to 100° with sulfuric acid for three hours. The hydrocarbons dissolved and the solutions became very dark, but no evidence of any rearrangement was observed. Hydrolysis of the sulfonic acids in the solutions yielded the original hydrocarbons in 87% (1,2,4) and 60% (1,3,5) yields. The regenerated hydrocarbons were identified by conversion to the tribromo derivatives which melted, without purification, within one degree of the pure substances. This result was not unexpected, for no trialkylbenzene so far investigated has been found to undergo the Jacobsen rearrangement.

The tetraethylbenzenes, when subjected to the conditions of the Jacobsen rearrangment, paralleled in behavior the tetramethylbenzenes. 1,2,4,5- and 1,2,3,5-tetraethylbenzenes first sulfonated and then the sulfonic acids rearranged. The product from both was the sulfonic acid of 1,2,3,4-tetraethylbenzene. But in contrast to the behavior of the tetramethyl compounds, rearrangement of the ethyl analogs was remarkably rapid and smooth. The yield of 1,2,3,4-tetraethylbenzene sulfonic acid was 90–92% and the reaction was completed in fifteen minutes at 100°. The tarry, polymeric by-product, present in the products of all Jacobsen rearrangements studied so far, was entirely absent and little or no sulfur dioxide was evolved during the reaction. Moreover, the resulting sulfonic acid was much more resistant to action of sulfuric acid than was prehnitene sulfonic acid.[6] It was smoothly hydrolyzed in acid solution at 140°, and the hydrocarbon readily could be obtained from it in yields of 90% or better. Over-all yields of 85–88% frequently were obtained in the conversion of either of the other tetraethylbenzenes, or a mixture of them, into the 1,2,3,4-isomer by these procedures.

Pentaethylbenzene was converted into the sulfonic acid in 89% yield by action of chlorosulfonic acid. This sulfonic acid was very readily hydrolyzed to the hydrocarbon by concentrated sulfuric acid at room temperature. By heating the hydrocarbon with sulfuric acid for two hours at 100°, the sulfonic acid was not so extensively hydrolyzed and under these conditions it slowly underwent a Jacobsen rearrangement. The rearrangement, like that of pentamethylbenzene, was an intermolecular one, leading to hexaethylbenzene and 1,2,3,4-tetraethylbenzene. The yields were poor, however, and much tarry material resulted along with a copious evolution of sulfur dioxide. Use of fuming sulfuric acid did not lead to any better results, the rearrangement products, produced in poor yields, were the same as before, and there was the same copious evolution of sulfur dioxide accompanied by formation of large amounts of the dark, amorphous polymeric by-product.

Thus, as far as the nature of the products is concerned, the Jacobsen rearrangement of polyethylbenzenes is strictly analogous to that of polymethylbenzenes. The ease with which the rearrangements occur in the two series is strikingly different, however; while the tetraethylbenzenes rearrange much more smoothly and quickly than do the tetramethylbenzenes, the reverse is true in the case of the pentaalkylbenzenes; in this case the methylbenzene rearranges more readily, and gives better yields of products than does the ethylbenzene.

(4) Galle, *Ber.*, **16**, 1744 (1883).

(5) Dillingham and Reid, THIS JOURNAL, **60**, 2606 (1938).

(6) Smith and Lux, *ibid.*, **51**, 2994 (1929).

Experimental Part[7]

Jacobsen Reactions of Triethylbenzenes.—**1,2,4-Triethylbenzene** (30 g.) was stirred with sulfuric acid (100 g.) at 100° for three hours. The hydrocarbon dissolved completely. The dark solution was poured over ice and then steam distilled until the temperature of the liquid rose to 170°. The distillate contained 26 g. (87%) of oil which was identified as 1,2,4-triethylbenzene by conversion to the tribromo derivative. The starting material (5 g.) when brominated at 0° gave 8.85 g. of tribromo derivative melting at 86–87° after crystallization from alcohol; the product (5 g.) gave 7.5 g. of tribromo derivative melting at 86–87°.[8]

1,3,5-Triethylbenzene (30 g.), when subjected to the above procedure, gave a steam distillate which contained 18 g. (60%) of oil, identified as 1,3,5-triethylbenzene by conversion to the tribromo derivative melting at 99–102°. The starting material gave the same tribromo compound, melting at 100–102°.[9] The difference in ease of bromination of these two triethylbenzenes was very marked. The 1,2,4-isomer was brominated readily and the tribromo compound resulted in good yield, while the 1,3,5-isomer was brominated much more difficultly and the product was formed in relatively poor yields.

Jacobsen Reactions of Tetraethylbenzenes.—Since preliminary experiments upon the ethylation mixture of 1,2,4,5- and 1,2,3,5-tetraethylbenzenes showed that the sole product of the reaction was the 1,2,3,4-isomer, and that over 85% of the material could be accounted for, most of the subsequent experiments were also carried out directly upon this mixture. The mixed tetraethylbenzenes (25 g., b. p. 110–113°, under 10–11.5 mm.) were stirred at 100° with sulfuric acid (100 g.) for fifteen minutes. The emulsion, which first resulted, was yellow and then the color darkened somewhat and the hydrocarbons dissolved completely. The cooled solution was poured over crushed ice (about 100 g.). The (tan colored) sulfonic acid crystallized when the mixture was cooled in an ice-bath. It was removed and crystallized from a mixture of benzene and petroleum ether (b. p. 60–68°). The white product weighed 34–35 g. (90.7–92.3%) and melted, after drying in a desiccator over calcium chloride, at 118–120°. The sulfonic acid contained one molecule of crystal water.

Anal. Calcd. for $C_{14}H_{24}O_4S$: C, 58.28; H, 8.39; neut. equiv., 288.2. Found: C, 58.04; H, 8.40; neut. equiv., 286.3, 286.6.

Sulfonamide.—The sulfonic acid (2 g.) was dissolved in phosphorus oxychloride (12 cc.), phosphorus pentachloride (4 g.) was added and the solution was heated on the steam-bath for thirty minutes. Ice was added and the sulfonyl chloride was removed by ether extraction. Ammonium hydroxide (50 cc.) was added to the ether solution and the ether was evaporated. The amide was removed and crystallized from dilute ethanol. It formed white plates which melted at 103–105°.[3,4,10]

Anal. Calcd. for $C_{14}H_{23}O_2NS$: C, 62.40; H, 8.61. Found: C, 62.38; H, 8.85.

Sulfonanilide.—Prepared from the sulfonic acid (1 g.) as above, substituting aniline (1 cc.) for the ammonia. The anilide, after crystallization from dilute ethanol, melted at 120–121°.

Anal. Calcd. for $C_{20}H_{27}O_2NS$: C, 69.52; H, 7.88. Found: C, 69.70; H, 8.11.

1,2,3,4-Tetraethylbenzene.—The sulfonic acid (84 g., 0.29 mole, m. p. 118–120°) obtained from the Jacobsen reaction was added to sulfuric acid (300 cc., 50%). The solution was heated while steam was passed through it (thermometer in the liquid). At 100° there was no hydrolysis, but at 130° hydrolysis began and at 140–150° it was quite rapid. No tarry residue was formed, and only a light brown color developed during the hydrolysis. The oil in the distillate was removed, dried over calcium chloride, and distilled through a Fenske column,[11] 25″ × 3/4″ packed with 1/8″ glass helices and equipped with an electrically heated jacket. The hydrocarbon distilled completely at 119–120° under 11 mm., did not solidify when cooled in a bath of acetone and dry-ice, and had all of the other physical properties of 1,2,3,4-tetraethylbenzene.[1a] The yield was 50 g. (90.7%).

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 88.33; H, 11.37.

It was not necessary to isolate and purify the sulfonic acid in order to obtain a pure product from these Jacobsen rearrangements. The general procedure used for *preparation* of 1,2,3,4-tetraethylbenzene was as follows: the tetraethylbenzene fraction from the ethylation of benzene, or the filtrate after the sym-hydrocarbon had been frozen out of this fraction, was stirred with three and one-half to four times its weight of sulfuric acid at 95–105° until solution was complete (about fifteen minutes). The solution was poured onto sufficient crushed ice so that the sulfuric acid was diluted to about 50% by volume, and then steam was passed through the mixture at 140–150°. The oil in the distillate was fractionated as above. The results of three such experiments are given in the table. In the first experiment, the starting material was a tetraethylbenzene fraction (b. p. 110–113° under 9–10.5 mm.) free from other ethylated benzenes; in the other two experiments, the starting material contained some lower boiling triethylbenzenes.[12]

TABLE I

PREPARATION OF 1,2,3,4-TETRAETHYLBENZENE

IV fraction, g.	Sulfuric acid, g.	Product, g.	Yield, %
100	368	88	88
190	700	140	73.7
210	700	175	83.3

Jacobsen Rearrangement of 1,2,4,5-Tetraethylbenzene Sulfonic Acid.—To show that it was the sulfonic acid, and not the hydrocarbon, which rearranged, the pure sulfonic acid of 1,2,4,5-tetraethylbenzene (2 g., m. p. 105–107°)[13] was added to sulfuric acid (10 cc.) and the mixture was

(7) Some of the microanalyses are by E. E. Renfrew and E. E. Hardy.

(8) Klages and Keil, *Ber.*, **36**, 1632 (1903), give the m. p. as 88–90°.

(9) (a) Gustavson, *J. prakt. Chem.*, [2] **68**, 209 (1903), reports the m. p. of this compound as 103.5–104°; (b) Norris and Ingraham, THIS JOURNAL, **60**, 1422 (1938), report 104.6–104.8°; (c) Gattermann, Fritz and Beck, *Ber.*, **32**, 1122 (1899), report 105–106°.

(10) Jacobsen (ref. 3) gives the m. p. as 107°; Galle (ref. 4) gives 104–105°.

(11) Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, **26**, 1169, 1213 (1934); *ibid.*, **29** 957 (1937).

(12) The authors are greatly indebted to the Dow Chemical Company for a generous gift of various polyethylbenzene fractions.

(13) Paper XXVII, THIS JOURNAL, **62**, 2625 (1940).

shaken and heated to 100°. The solution was immediately poured over ice and the sulfonic acid isolated and crystallized from benzene–petroleum ether (b. p. 60–68°). It weighed 1.5 g. (75%) and melted at 117–119° alone or when mixed with the sulfonic acid of 1,2,3,4-tetraethylbenzene. The rearrangement was extremely rapid at 100°, but even at room temperature considerable change occurred. A duplicate of the above experiment, except that it was carried out for two hours at room temperature, yielded 0.12 g. of 1,2,3,4-tetraethylbenzene sulfonic acid.

Pentaethylbenzene Sulfonic Acid.—Pentaethylbenzene (10 g.) was added dropwise and with shaking to chlorosulfonic acid (50 g.). Unless a solvent were used, a great excess of chlorosulfonic acid was necessary in order to prevent solidification of the reaction mixture before the reaction was complete. When the hydrocarbon was dissolved in carbon tetrachloride (100 cc.), a weight of chlorosulfonic acid equal to that of the hydrocarbon could be used. The product in either case was poured over ice, extracted with ether and the solvents removed. To the residue was added sodium hydroxide (10 g.) in sufficient water (100 cc.) to dissolve completely at 90° the sodium sulfonate. The solution, when cooled, precipitated the salt which could be recrystallized from water. However, the cooled suspension of the crude salt was usually acidified with excess sulfuric acid until the concentration of sulfuric acid reached 30–50%; from the cold mixture, the sulfonic acid crystallized. It was removed and recrystallized from benzene–petroleum ether (b. p. 60–68°), when it formed long, voluminous, slender white needles melting at 113–115°. It crystallized with one molecule of crystal water. The yield was 12.9 g. (89%).

Anal. Calcd. for $C_{16}H_{28}O_4S$: C, 60.71; H, 8.92; neut. equiv., 316.3. Found: C, 60.56; H, 8.80; neut. equiv., 321.

Pentaethylbenzene Sulfonyl Chloride.—The sulfonic acid (2 g.) was dissolved in phosphorus oxychloride (10 cc.) and phosphorus pentachloride (3 g.) was added. After heating the solution for thirty minutes, it was poured over ice and the solid product was removed and crystallized from aqueous dioxane. It melted at 137–138°.

Anal. Calcd. for $C_{16}H_{25}O_2SCl$: C, 60.62; H, 7.96. Found: C, 61.23; H, 7.95.

Anilide.—To a solution of the sulfonyl chloride from 2 g. of hydrocarbon, prepared as above but with the addition of dioxane (20 cc.) to the reaction mixture (without isolation of the product), there was added 1.25 cc. of aniline. The solution was heated on the steam-bath for twenty minutes and then diluted with water. The solid anilide was removed and crystallized from aqueous ethanol. It formed white needles (1.3 g.) which melted at 140–141°.

Anal. Calcd. for $C_{22}H_{31}O_2NS$: C, 70.72; H, 8.37. Found: C, 70.52; H, 8.05.

Ethyl Pentaethylbenzene Sulfonate.—In various experiments made to prepare the amide or anilide from the chloride in water, it was found that the product, after crystallization from aqueous alcohol, melted at 70–71° whether ammonia or aniline had been used. When the sulfonyl chloride was crystallized from aqueous ethanol, the same product resulted. Curiously enough, the sulfonyl chloride was recovered unchanged after it was warmed on the steam-bath for thirty minutes with concd. aqueous ammonia.

Anal. Calcd. for $C_{18}H_{30}O_3S$: C, 66.20; H, 9.27. Found: C, 66.24; H, 9.32.

Hydrolysis of the Sulfonic Acid.—The acid (10 g.) was shaken with sulfuric acid (50 cc.) at room temperature for five to ten minutes. A clear supernatant oil was formed. The mixture was poured over ice and extracted with ether. The ether solution was dried over calcium chloride and the solvent was removed by distillation through a short packed column. The residue was then distilled. The distillate was pentaethylbenzene (6.5 g., 94%), boiling at 140–145° under 17 mm. A portion of the distillate, sulfonated with chlorosulfonic acid as described above, gave pentaethylbenzene sulfonic acid, m. p. and mixed m. p. 113–115°. The hydrolysis of the sulfonic acid by sulfuric acid occurred also at temperatures below that of the room, but at a slower rate.

Jacobsen Rearrangement of Pentaethylbenzene.—The hydrocarbon (30 g.) was added to sulfuric acid (75 cc.) and the mixture was stirred and heated to 100° for two hours. The very dark reaction mixture was cooled and poured over ice. The solid was removed and crystallized from aqueous ethanol. It was hexaethylbenzene (3.1 g.), m. p., and mixed m. p., 126–128°. The aqueous filtrate was steam distilled at 170°. There resulted 12 g. of oil which by fractionation through a short, packed column was separated into a tetraethylbenzene (4.5 g.) and pentaethylbenzene (7.5 g.). The tetraethylbenzene was identified as the 1,2,3,4-isomer by conversion to the dibromo derivative, m. p. and mixed m. p. 73–75°.

When the method of Jacobsen[3] was used, the results were not better, but worse. The hydrocarbon (25 g.) was added in the cold to an equal volume of sulfuric acid, and sufficient fuming sulfuric acid was added to effect complete solution. After standing for four days at room temperature, the reaction mixture was processed as above. There resulted 3.5 g. of hexaethylbenzene, but no oil whatever could be obtained from the filtrate by steam distillation at 170°. When conducted by either method, this Jacobsen reaction produces large amounts (over 50%) of tarry, polymeric by-products, and gives rise to large amounts of sulfur dioxide.

Summary

1. Two triethylbenzenes, 1,2,4- and 1,3,5-, when subjected to conditions of the Jacobsen rearrangement, are recovered unchanged.

2. Two tetraethylbenzenes, 1,2,4,5- and 1,2,3,5-, undergo the Jacobsen rearrangement with extreme ease. The product from either or both is the sulfonic acid of 1,2,3,4-tetraethylbenzene; the yield is about 90% and there are no tarry by-products formed.

3. The sulfonic acid of 1,2,3,4-tetraethylbenzene can be smoothly hydrolyzed to the hydrocarbon in yields of 90%. This process, when combined with the methods of separation previously reported for the other two tetraethylbenzenes, completes the series of preparative methods for the three pure tetraethylbenzenes.

4. Pentaethylbenzene undergoes the Jacobsen rearrangement with extreme difficulty. The products are hexaethylbenzene and 1,2,3,4-tetraethylbenzene sulfonic acid, but the yields are poor and the reaction is accompanied by large amounts of tarry by-products and sulfur dioxide.

5. Pentaethylbenzene sulfonic acid can be hydrolyzed to the hydrocarbon with extreme ease.

6. Several derivatives of pentaethylbenzene sulfonic acid, and 1,2,3,4-tetraethylbenzene sulfonic acid, are described.

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Polyalkylbenzenes. XXX.[1] Nitration of Tetra-, Penta- and Hexa-ethylbenzenes; Bromination of the Tetraethylbenzenes

BY LEE IRVIN SMITH AND CYRUS O. GUSS[2]

Nitration of polyalkylbenzenes is of interest not only because the reaction provides good derivatives for identification of these hydrocarbons, but also because of the curious attack upon the side chain, leading to the formation of nitrates, which often accompanies it.[3] Bromination, on the other hand, while a smooth reaction, does not lead to good derivatives in the polymethylbenzene series, because the isomeric polybromo derivatives of these hydrocarbons show little or no depression in melting points when mixed.[4,5] In recent papers[1,6] methods have been described by means of which it is possible to conduct the ethylation of benzene efficiently to any desired stage. Methods for the separation of isomeric hydrocarbons and for preparation of 1,2,3,4-tetraethylbenzene also have been described. By combination of these procedures it is possible to prepare in some quantity any of the pure polyethylbenzenes except for 1,2,3-triethylbenzene. With adequate amounts of pure hydrocarbons at hand, it was of interest to examine the nitration and bromination of five polyethylbenzenes, the three tetraethylbenzenes, penta- and hexa-ethylbenzenes, and to compare the reactions as well as the products, with those of the corresponding polymethylbenzenes.

Very little is to be found in the literature concerning nitration of polyethylbenzenes. Galle[7] reported that nitration of 1,2,3,4-tetraethylbenzene gave a dinitro compound which melted at 115°; he also reported that hexaethylbenzene gave, in poor yield, a dinitrotetraethylbenzene in which the two nitro groups were para to each other, a fact which was also reported later by Jannasch and Bartels[8] and verified by Smith and Harris.[9]

Nitration of hexaethylbenzene has been repeated, and the previous conclusions as to the nature of the solid product have been verified. In the newer experiments, the yield was improved slightly (from 13 to 17%), but the only solid which could be isolated from the oily reaction mixture was *p*-dinitrotetraethylbenzene melting at 145–147°. It was identified by conversion to tetraethyl-*p*-benzoquinone via the diamine.[9]

Nitration of pentaethylbenzene under the same conditions produced the same *p*-dinitrotetraethylbenzene in nearly 70% yield. This reaction constitutes the simplest and best preparative method for this dinitro compound, and through it, for the corresponding diamine and parabenzoquinone.

The difference in the orientation of the dinitro compounds produced from the polymethyl and polyethyl benzenes is very striking. Both of the hexaalkylbenzenes give dinitro compounds; the yields are poor, 17% in the ethyl series and 22%[9] in the methyl series, but the orientation of the solid product is entirely para in the ethyl series and entirely ortho in the methyl series. When the pentaalkylbenzenes are nitrated, the yields in both series are excellent (over 70%), but again the orientation in the methyl series is entirely ortho[9] while in the ethyl series it is entirely para.

Nitration of 1,2,4,5-tetraethylbenzene gave the *p*-dinitro compound, melting at 145–147°, in 61% yield. Nitration of this tetraethylbenzene, therefore, did not constitute as good a preparative method for its dinitro compound as did nitration

(1) XXIX, THIS JOURNAL, **62**, 2631 (1940).

(2) Abstracted from a thesis by Cyrus O. Guss, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) Smith and Horner, THIS JOURNAL, **62**, 1349 (1940).

(4) Smith and Moyle, *ibid.*, **55**, 1676 (1933).

(5) Smith and Kiess, *ibid.*, **61**, 989 (1939).

(6) Smith and Guss (a) *ibid.*, **62**, 2625 (1940); (b) **62**, 2631 (1940).

(7) Galle, *Ber.*, **16**, 1744 (1883).

(8) Jannasch and Bartels, *ibid.*, **31**, 1717 (1898).

(9) Smith and Harris, THIS JOURNAL, **57**, 1289 (1935).