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

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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

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[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).

of pentaethylbenzene. The reverse is true in the methyl series; here the yield of dinitrodurene from durene is often 90%. The production of a para dinitro compound from the tetraethylbenzene which melted at 10° definitely fixed the structure of this hydrocarbon; it could be no other than the 1,2,4,5-tetraethylbenzene. Moreover, the reaction showed that in the nitration of this hydrocarbon, no rearrangements of the alkyl groups were involved.

The tetraethylbenzene resulting from the Jacobsen rearrangement of the other two isomers, and regarded as the 1,2,3,4-isomer, gave in 68% yield a dinitrotetraethylbenzene which melted at 117–118°. This dinitro compound, when reduced, gave a diamine melting at 69–70° which was an *ortho* diamine because it could be converted into a phenanthrophenazine with phenanthraquinone, and into a benzimidazole with acetic acid. Hence this tetraethylbenzene was the 1,2,3,4-isomer, and, when nitrated, again no rearrangements of the alkyl groups occurred.

The third tetraethylbenzene therefore was the 1,2,3,5-isomer. It gave a dinitro compound which melted at 93.5-94.5°, but the yield of purified product was only 35%.

As in the tetramethylbenzene series, the dinitrotetraethylbenzenes were good solid derivatives of the hydrocarbons; the melting point depressions of binary mixtures (about 50-50) of the three dinitro compounds are shown in Table I.

TABLE I

MELTING POINTS OF BINARY MIXTURES OF DINITROTETRAETHYLBENZENES

Dinitrotetraethylbenzenes	M. p. of mixture, °C.
vic (117–118°) + *sym* (145–147°)	105–109
vic + *unsym* (93.5–94.5°)	80–86
sym + *unsym*	88–91

But one monobromotetraethylbenzene has been described in the literature. This is 5-bromo-1,2,3,4-tetraethylbenzene, which boils at 284° and which was reported by Galle[7] and by Klages and Keil.[10] Two dibromotetraethylbenzenes are known. Jacobsen[11] reported the melting point of 3,6-dibromotetraethylbenzene as 112.5°; Klages and Keil[10] reported 113°, while Galle[7] reported 110°. 5,6-Dibromotetraethylbenzene was first reported by Jacobsen,[11] who gave the melting point as 77°; later, Klages and Keil[10] reported that the substance melted at 74.5°.

The monobromo derivatives of the tetraethylbenzenes were conveniently prepared (92–96% yields) by direct bromination of the hydrocarbons at room temperature in chloroform or acetic acid. These substances were all colorless liquids at room temperature. 3-Bromo-1,2,4,5-tetraethylbenzene melted at 9°; the other two monobromo compounds did not solidify at the temperature of a mixture of acetone and dry-ice. Two of the monobromo compounds, those from the *sym*- and *unsym*-hydrocarbons, had the same refractive index at 20°, $n^{20}\text{D}$ 1.5425.

The dibromo derivatives were likewise prepared (87–95% yields) from the hydrocarbons by direct bromination, but it was important that chloroform, and not acetic acid, be used as the solvent. In the latter solvent, reaction did not proceed well (30% yield) beyond the monobromo stage because the monobromo compound separated from acetic acid as soon as much of it was formed. The dibromo compounds were all white solids whose binary mixtures, with one exception, showed small but definite melting point depressions although the melting point range was in every case quite wide. In this respect the dibromo compounds are better derivatives of the tetraethylbenzenes than of the tetramethylbenzenes,[4,5] but, even so, the melting point depressions leave much to be desired and the dinitro compounds, though not formed from the hydrocarbons in such excellent yields, are for most purposes better derivatives since they give greater depressions and narrower melting point ranges. The melting point depressions of binary mixtures (about 50–50) of the three dibromotetraethylbenzenes are given in Table II.

TABLE II

MELTING POINTS OF BINARY MIXTURES OF DIBROMOTETRAETHYLBENZENES

Dibromotetraethylbenzenes	M. p. of mixture, °C. Softens	Collapses	Last solid disappears
vic (76–77°) + *unsym* (48–49.5°)	43–44	45–47	73
sym (112–113°) + *unsym*	46–47	49	95
vic + *sym*	68–69	70–71	93–94

When 3,6-dibromotetraethylbenzene was nitrated, a substance containing halogen and nitrogen, and melting at 120–122°, was obtained. This reaction is similar to that shown by dibromodurene on nitration[12] and which leads to the

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[10] Klages and Keil, *Ber.*, **36**, 1632 (1903).

[11] Jacobsen, *ibid.*, **21**, 2814, 2819 (1888).

[12] (a) Smith and Tenenbaum, THIS JOURNAL, **57**, 1293 (1935); (b) Smith, Taylor and Webster, *ibid.*, **59**, 1082 (1937); (c) Smith and Horner, *ibid.*, **62** 1349 (1940).

formation of 3,6-dibromo-2,4,5-trimethylbenzyl nitrate. The structure of the product from dibromotetraethylbenzene is still under investigation; the work so far, although not decisive, indicates that this product is a dibromotriethylbenzyl nitrate, *i. e.*, one carbon atom has been removed from an ethyl group during the reaction. Galle[7] and also Jannasch and Bartels[8] have reported that a somewhat similar change occurs when hexaethylbenzene is brominated in the presence of iodine; the product is 3,6-dibromotetraethylbenzene, m. p. 112.5°.

Experimental Part[13]

Nitrations. Hexaethylbenzene.—The hydrocarbon (10 g.) was dissolved in chloroform (90 cc.) and added to sulfuric acid (72 cc.). The mixture was well stirred and cooled (-5 to $-10°$) and fuming nitric acid (d. 1.5, 20 cc.) was added fairly rapidly (thirty minutes). The mixture darkened at first, and then became light yellow toward the end of the reaction. Ice water was added and the chloroform layer was removed and washed with water, sodium carbonate, and again with water. The solvent was evaporated and the last traces of it were removed under reduced pressure. The oily residue, when dissolved in alcohol and cooled, yielded 1.95 g. (17%) of **3,6-dinitrotetraethylbenzene**, m. p. and mixed m. p. 145–147°.

Pentaethylbenzene.—The hydrocarbon (10 g.) was nitrated as described above. The product weighed 8.98 g. (69.7%) and was **3,6-dinitrotetraethylbenzene**, m. p. and mixed m. p. 145–147°. When the hydrocarbon was added to the nitrating mixture, the yield of dinitro compound dropped to 16%.

1,2,4,5-Tetraethylbenzene.—The hydrocarbon (10 g.) was nitrated as above, using chloroform (60 cc.), sulfuric acid (45 cc.) and fuming nitric acid (d. 1.5, 8 cc.) at 0°. The product (9 g., 61%) was **3,6-dinitrotetraethylbenzene**, m. p. and mixed m. p. 145–147°.

Tetraethyl-*p*-benzoquinone.—To a hot solution of the above dinitro compound (4 g.) in acetic acid (35 cc.) was added a solution of stannous chloride dihydrate (25 g.) in hydrochloric acid (30 cc.). After the vigorous reaction subsided, the mixture was heated for ten minutes and then cooled to 0°. The diamine stannichloride was filtered off and washed with alcohol and ether. The salt was decomposed by excess sodium hydroxide (20%); the diamine was filtered off and dissolved in excess ferric chloride solution. Steam distillation of this solution gave a distillate containing 2.3 g. (73%) of tetraethylquinone, melting at 58–59° after crystallization from dilute alcohol.[9]

1,2,3,5-Tetraethylbenzene.—The hydrocarbon (10 g.), when nitrated by the same procedure used for its isomer, gave 5.5 g. (35%) of **4,6-dinitro-1,2,3,5-tetraethylbenzene.** After crystallization from dilute alcohol, the substance formed light yellow needles which melted at 93.5–94.5°.

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: C, 59.97; H, 7.20. Found: C, 60.05; H, 7.09.

1,2,3,4-Tetraethylbenzene.—The hydrocarbon (10 g.), nitrated in the same manner as used for the other tetraethylbenzenes, gave 10.5 g. (68%) of **5,6-dinitro-1,2,3,4-tetraethylbenzene.** After crystallization from alcohol, the substance formed light yellow needles which melted at 117–118° (Galle[7] reports the m. p. as 115°).

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: C, 59.97; H, 7.20. Found: C, 59.87; H, 7.34.

5,6-Diamino-1,2,3,4-tetraethylbenzene.—The above dinitro compound (4 g.) was dissolved in hot ethanol (35 cc.), and a hot solution of stannous chloride dihydrate (25 g.) in hydrochloric acid (30 cc.) was added. The reduction was very rapid; after the initial reaction moderated, the mixture was refluxed for an hour, then cooled and poured into excess sodium hydroxide solution (20%). The diamine (2.5 g.) was filtered off and crystallized from dilute alcohol. The substance was purified with difficulty, for the solid as well as its solutions became colored on standing in air. What appeared to be the best sample melted at 69–70°.

Anal. Calcd. for $C_{14}H_{24}N_2$: C, 76.30; H, 10.98. Found: C, 75.71; H, 10.78.

10,11,12,13-Tetraethylphenanthrophenazine.—A hot solution of phenanthraquinone in acetic acid was added to an alcoholic solution of the above diamine and the mixture was heated on the steam-bath for five minutes. The phenazine was removed from the cooled mixture and recrystallized from ethanol. It formed fine yellow needles which melted at 169–170°.

Anal. Calcd. for $C_{28}H_{28}N_2$: C, 85.67; H, 7.20. Found: C, 85.56; H, 7.37.

4,5,6,7-Tetraethyl-2-methylbenzimidazole.—To a solution of 5,6-dinitro-1,2,3,4-tetraethylbenzene (2 g.) in acetic acid (20 cc.) was added a hot solution of stannous chloride dihydrate (15 g.) in hydrochloric acid (20 cc.), and the mixture was refluxed for two hours. Excess sodium hydroxide solution (20%) was added and the solid was removed and crystallized from dilute ethanol. It was white and melted at 241–242°.

Anal. Calcd. for $C_{16}H_{24}N_2$: C, 78.62; H, 9.91. Found: C, 78.58; H, 9.86.

Brominations.—The general procedure for preparation of **monobromotetraethylbenzenes** was as follows: the hydrocarbon (20 g., 0.105 mole) and a crystal of iodine were dissolved in chloroform (50 cc.) and to the stirred solution was added liquid bromine (18 g., 0.113 mole). The reaction mixture was shielded somewhat from the light, but it was not cooled and the bromine was added at such a rate that the temperature did not rise appreciably. The reaction mixture was stirred for an hour longer, then the solution was washed successively with water, sodium bisulfite and again with water. After drying the solution over calcium chloride, the solvent was distilled off and the residue was fractionated through a short packed column. The products were colorless liquids, and the yields were 26–27 g. (92–96%).

3-Bromo-1,2,4,5-tetraethylbenzene.—B. p. 149° under 9 mm., 151° under 10 mm.; n^{20}_{D} 1.5425; m. p. 9°, determined by the freezing point method on a relatively large sample. Figure 1 shows the cooling curve.

Anal. Calcd. for $C_{14}H_{21}Br$: C, 62.44; H, 7.87. Found: C, 62.65; H, 7.72.

4-Bromo-1,2,3,5-tetraethylbenzene.—B. p. 150° under 9 mm., 156° under 13 mm., 158° under 15 mm., n^{20}_{D} 1.5425.

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[13] Most of the microanalyses are by E. E. Renfrew.

Anal. Calcd. for $C_{14}H_{21}Br$: C, 62.44; H, 7.87. Found: C, 62.35; H, 7.82.

5-Bromo-1,2,3,4-tetraethylbenzene.—B. p. 152° under 9 mm., 158° under 13 mm.; $n^{20}D$ 1.5453.

Anal. Calcd. for $C_{14}H_{21}Br$: C, 62.44; H, 7.87. Found: C, 62.45; H, 7.42.

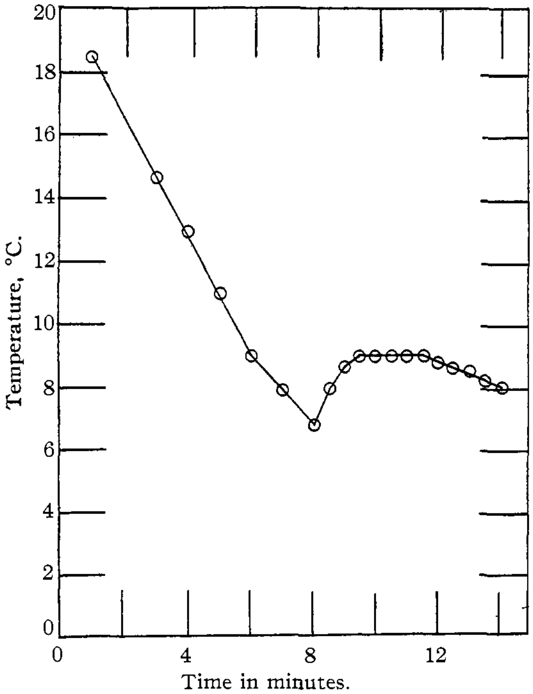

Fig. 1.—Cooling curve of 3-bromotetraethylbenzene.

The general procedure for preparation of the **dibromotetraethylbenzenes** was as follows: liquid bromine (19 g., 0.12 mole) was added to a solution of the hydrocarbon (10 g., 0.056 mole) in chloroform (50 cc.) containing a crystal of iodine. The reaction was carried out at room temperature, in the absence of any strong light, and the reaction mixture was allowed to stand overnight. The chloroform solution was processed as for the monobromo compounds; the residue after removal of the solvent was crystallized from alcohol or (and better for the *sym*-compound) alcohol–chloroform. The products all crystallized in the form of white needles; the yields were 17–18.5 g. (87–95%). When acetic acid was used as the solvent in place of chloroform, the yields of dibromo compounds were much less. Thus in one experiment the *sym*-hydrocarbon, brominated in acetic acid, gave 6 g. (31%) of dibromo compound. Acetic acid could be used as the solvent when monobromo compounds were desired, but these separated from the solvent as the reaction progressed and were thus kept from further contact with bromine. When dibromo compounds were desired, it was quite important that chloroform be used as the solvent.

3,6-Dibromo-1,2,4,5-tetraethylbenzene melted at 112–113°.

Anal. Calcd. for $C_{14}H_{20}Br_2$: C, 48.28; H, 5.79. Found: C, 48.20; H, 5.87.

4,6-Dibromo-1,2,3,5-tetraethylbenzene melted at 48–49.5°.

Anal. Calcd. for $C_{14}H_{20}Br_2$: C, 48.28; H, 4.79. Found: C, 48.54; H, 5.60.

5,6-Dibromo-1,2,3,4-tetraethylbenzene melted at 76–77°.

Anal. Calcd. for $C_{14}H_{20}Br_2$: C, 48.28; H, 5.79. Found: C, 48.23; H, 5.59.

Nitration of 3,6-Dibromo-1,2,4,5-tetraethylbenzene.—The dibromo compound (10 g.) was dissolved in chloroform (90 cc.) and the solution was stirred with sulfuric acid (72 cc.) at −5 to −10°. Fuming nitric acid (d. 1.5, 15 cc.) was added slowly at such a rate that the temperature did not rise above 0°. The reaction mixture was processed immediately as described above for the nitration of hexaethylbenzene. After removal of the chloroform, the residue was crystallized from dilute ethanol. It weighed 2.5 g. and formed light yellow needles which melted at 120–122°.

Anal. Calcd. for $C_{14}H_{19}O_3NBr_2$ (nitrate of a phenyl ethanol): C, 41.07; H, 4.64. Calcd. for $C_{13}H_{17}O_3NBr_2$ (nitrate of a benzyl alcohol): C, 39.50; H, 4.30. Found: C, 39.95; H, 4.62.

Summary

1. The nitration of five polyethylbenzenes has been studied and the structures of the products have been proved. Each of the tetraethylbenzenes gives the corresponding dinitro compound, with no rearrangement.

2. Hexaethylbenzene and pentaethylbenzene both give para dinitrotetraethylbenzene, the latter hydrocarbon giving the dinitro compound in 70% yield. This is the best preparative method so far found for this dinitrotetraethylbenzene. These two polyethylbenzenes differ sharply from the corresponding polymethylbenzenes on nitration, for in the latter case *ortho* dinitrotetramethylbenzenes are formed.

3. The mono- and di-bromo derivatives of the three tetraethylbenzenes have been prepared and characterized.

4. As previously found in the case of tetramethylbenzenes, the dinitrotetraethylbenzenes are good solid derivatives of the hydrocarbons. Binary mixtures of the dinitro compounds show good melting point depressions and fairly narrow melting point ranges. Binary mixtures of the dibromo compounds, however, show only slight melting point depressions and have very wide melting point ranges.

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