[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Hyperconjugation. IV. The Bromination of Additional Monoalkylbenzenes[†]

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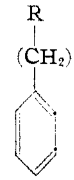
The relative rates of bromination of alkylbenzenes depend, to a predominant extent, upon the number of hydrogens on the carbon atom *alpha* to the benzene ring.[1,2] First-order hyperconjugation of these *alpha* hydrogen atoms with the aromatic nucleus can account for the established order of reactivity toluene > ethylbenzene > etc., (series I, Fig. 1) where three, two, one and no *alpha* hydrogens are available for conjugation with the ring.[3,4] Analogously, when the number of *alpha* hydrogens is constant (Series II), second-order hyperconjugation can account for the decrease in relative rates of bromination with decrease in the number of *beta* hydrogens.[1]



R = Me, Et, *i*-Pr, *t*-Bu

Series I, *n* = 0 Series III, *n* = 2
Series II, *n* = 1 Series IV, *n* = 3
Series V, *n* = 4

Fig. 1

In the present investigation, the study of the relative rates of bromination of monoalkylbenzenes has been extended in order to evaluate the effect of hydrogen atoms further removed along the aliphatic chain. The compounds studied include four amylbenzenes—2-phenylpentane, 3-phenylpentane, isoamylbenzene, and α-benzylbutane[5]—*n*-hexylbenzene, isohexylbenzene, neohexylbenzene (1-phenyl-3,3-dimethylbutane) and neoheptylbenzene (1-phenyl-4,4-dimethylpentane). As in the previous investigation, the relative rates of bromination were established by comparing the times for ten per cent. reaction.[1,2,6]

Experimental Part[7]

Preparation of Materials

The **glacial acetic acid, 85% aqueous acetic acid, bromine** and **sodium acetate** used in these reactions have been previously described.[1]

Preparation of Neohexylbenzene (1-Phenyl-3,3-dimethylbutane)

Phenyl Neopentyl Ketone.—Mallinckrodt *t*-butylacetic acid[8] (n^{20}_{D} 1.4100; b. p. 184.2–184.5° (763–764 mm.) and 183.2–183.5° (754 mm.)) was converted to the acid chloride in 86 and 95% yields by treating the acid (0.4 mole and 0.6 mole, respectively) with a 20% excess of thionyl chloride at room temperature.[9] After the initial reaction had subsided, the reaction was completed by a short heating period on the water-bath (b. p. 81.2–82° (160 mm.), n^{25}_{D} 1.4208).

Seventy-six grams (0.565 mole) of the acid chloride, dissolved in 150 ml. of dry thiophene-free benzene, was slowly added through a dropping funnel to a suspension of 115 g. (0.86 mole) of aluminum chloride in 500 ml. of benzene contained in a three-necked flask equipped with stirrer and gas outlet tube. The addition took two hours, during which time the reaction mixture was cooled in ice. After that period the mixture was allowed to come to room temperature by letting it stand overnight. It was then worked up in the usual way. The yield of ketone boiling at 115.2–116.2° at 10–11 mm. was 87 g. (87%). In a second run on 0.34 mole of acid chloride a 90% yield of ketone boiling at 90–91° (4 mm.) was obtained. The ketone is a water-clear liquid with a sweet odor and boils at 245.2° (758 mm.), n^{20}_{D} 1.5078, n^{25}_{D} 1.5056, d^{25}_{25} 0.9512, d^{25}_{4} 0.9484. *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.50; H, 8.95. The melting point of the semicarbazone[10] depends on the rate of heating; samples of identical purity, crystallized from aqueous alcohol, melted sharply in the range 214 to 219°. A small sample, on rapid heating, melted at 214.4–215.4°. The highest melting point was 217.6–218.2°. *Anal.* Calcd. for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21. Found: C, 66.91; H, 8.27. The melting point of the oxime of phenyl neopentyl ketone[10] also depends on the rate of heating and is not well reproducible, probably because it sublimes in the neighborhood of its melting point. Crystallized from aqueous alcohol, it forms sharp white needles melting at 112.8–113.8° if the melting point is taken rapidly in a preheated bath. On slow heating it melts over a wider range (*e. g.*, 112.4–114°). *Anal.* Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.21; H, 8.94. Two samples of analytical purity, stored in glass vials, liquified after a short time. A sample left on filter paper in the open did not change its character. The crude 2,4-dinitrophenylhydrazone[10] of phenyl neopentyl ketone melts at about 108–114°. After several crystallizations from alcohol-chloroform mixtures, the bulk of the material forms dark orange, thick prisms melting at 157.6–158.2°. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66. Found: C, 60.38; H, 5.96. The mother liquors contained lower melting, lighter orange needles (m. p. 108–136°). This low melting material was converted into the higher melting form when its melting point was retaken several times or more rapidly, when the material was recrystallized several times from aqueous alcohol in the presence of a little hydrochloric acid. The lower melting crystals were not obtained in homogeneous form, but a sample melting from 119.5–136° had the right analysis for the 2,4-dinitrophenylhydrazone. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66. Found: C, 60.56; H, 5.77. The lower melting form is probably either a polymorphous form or a stereoisomer of the higher melting one. Since the melting point of the semicarbazone of phenyl neopentyl ketone is close to that reported for *t*-butylacetophenone,[11] it seemed advisable to compare the derivatives of both com-

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(†) Part of this material was presented before the Symposium on the Orientation of Substituents in Aromatic Systems at the 115th Meeting of the American Chemical Society in San Francisco, Cal., March 27–April 1, 1949.

(1) Berliner and Berliner, THIS JOURNAL, **71**, 1195 (1949).

(2) De la Mare and Robertson, *J. Chem. Soc.*, 279 (1943).

(3) Berliner and Bondhus, THIS JOURNAL, **68**, 2355 (1946).

(4) Baker and Nathan, *J. Chem. Soc.*, 1844 (1935).

(5) The other four amylbenzenes were studied in a previous investigation, ref. 1.

(6) Robertson, De la Mare and Johnston, *J. Chem. Soc.*, 276 (1943).

(7) All C and H analyses were done by Miss Margaret J. Quinn, Bryn Mawr College.

(8) We are greatly indebted to the Mallinckrodt Chemical Works, St. Louis, Mo., for a generous sample of *t*-butylacetic acid.

(9) Homeyer, Whitmore and Wallingford, THIS JOURNAL, **55**, 4209 (1933).

(10) Prepared according to directions in Shriner and Fuson, "The Systematic Identification of Organic Compounds," third edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

(11) Walther, *J. Pharm. Chim.*, [8] **27**, 476 (1938); *Chem. Abstr.*,

TABLE A

PREPARATION AND PROPERTIES OF MONOALKYLBENZENES[a,b]

Hydrocarbon	B. p., °C.	Mm.	$n^{20}D$	Acetamino deriv.[c] m. p., °C.
i-Amylbenzene[d]	195.4–196.1	753	1.4864	Mono 113.2–114.2
	196.4–197.1	763	1.4869	
1-Phenyl-2-methylbutane (2-benzylbutane)[e]	194.4–194.8	753	1.4885	Mono 116–116.8
				Di 198.6–199.6
2-Phenylpentane[f]	192.6–192.7	753	1.4881	Mono 105.5–106
3-Phenylpentane[g]	188.9–189	762	1.4879	Mono 145.6–146.4
n-Hexylbenzene[h]	223.8–224.6	757	1.4868	Mono 90.2–91.2[i]
				Di 201–202[j]
i-Hexylbenzene (1-phenyl-4-methylpentane)[k]	219–219.1	767	1.4853	Mono 106.4–107[l]
				Di 211.2–212.2[m]
Neohexylbenzene (1-phenyl-3,3-dimethylbutane)[n]	211.6–212	750	1.4826	Mono 160.6–161.2[n]
Neoheptylbenzene (1-phenyl-4,4-dimethylpentane)[n]	227.8–228.1	759	1.4832	Mono 107.4–108.4[n]

[a] For a summary of properties and syntheses of alkylbenzenes see Francis, *Chem. Revs.*, **42,** 107 (1948). [b] The alkylbenzenes recorded here and used in the bromination reactions were purified as previously described, see ref. 1. [c] Ipatieff and Schmerling, THIS JOURNAL, **59,** 1056 (1937); **60,** 1476 (1938); the melting points of the derivatives must be taken as indications of the identity rather than the purity of the hydrocarbons. [d] Prepared in 77% yield (b. p. 195.6–198° (761 mm.)) from 0.6 mole of *i*-valerophenone by a Wolff–Kishner reduction as modified by Huang-Minlon, THIS JOURNAL, **68,** 2487 (1946). The *i*-valerophenone was prepared in 90 and 92% yields from 0.78 and 0.83 mole of *i*-valeroyl chloride, benzene and aluminum chloride as described previously for similar ketones.[1] The ketone boiled at 142–143° (50 mm.) and 80–81° (3–4 mm.). The 2,4-dinitrophenylhydrazone formed dark red prisms when crystallized from ethanol–chloroform and melted at 131.8–132.8°; Evans and Gordon, *J. Chem. Soc.*, 1434 (1938), report a melting point of 131.5°. The oxime melted at 70.6–71.6° (lit. 72°, 74°). The crude semicarbazone melted at approximately 209°, but the melting point dropped on crystallization from aqueous ethanol (203.5–204.5°); lit. 209°, 210°. [e] Prepared in 82% yield by catalytic hydrogenation at room temperature of 1-phenyl-2-methylbutene-1, b. p. crude product 196–197° (762 mm.). The yield of pure product was 52%. The olefin was synthesized from 0.5 mole of benzaldehyde and *s*-butylmagnesium bromide (Glattfeld and Cameron, THIS JOURNAL, **49,** 1043 (1927)) in 54 and 63% yields. The crude product of the Grignard reaction (b. p. 175–192° (750 mm.)) was refluxed with iodine, washed with sodium bisulfite, sodium carbonate and water. A 34% yield of pure olefin boiling at 197–198° (756 mm.) was obtained and used for hydrogenation. [f] Prepared by catalytic reduction of 2-phenylpentene-2 in the presence of Raney nickel at room temperature. The yield of crude product, boiling at 190–191° (750 mm.) and 192–193.3° (763 mm.), was 86.5%; yield of pure product 44%. The olefin was synthesized from 0.5 mole of acetophenone and *n*-propylmagnesium bromide. The product of the reaction was refluxed for two hours without the addition of a dehydrating agent and distilled twice to complete the dehydration. The yield after two distillations was 63% (b. p. 197–200° (756 mm.)); see second ref. under [c] and Klages, *Ber.*, **35,** 3506 (1902). [g] Prepared by catalytic reduction of 3-phenylpentene-2 in the presence of Adams catalyst at room temperature. The yield of product boiling at 187–190° (763 mm.) was 83%. The olefin was prepared from 0.2 mole of propiophenone (b. p. 215.5° (745 mm.); m. p. 2,4-dinitrophenylhydrazone, 192.9–194.7°) and ethylmagnesium bromide in 65 and 79% yields, b. p. of crude product 196–201° (752 mm.); see second ref. under [c] and Klages, *Ber.*, **36,** 3688 (1903). [h] Prepared in 71.5% yield from 0.513 mole of caprophenone by the Huang modification of the Wolff–Kishner reduction (see first ref. in (*d*). Caprophenone was prepared in 73.5% yield (b. p. 132–134° (14 mm.); 258–260° (760 mm.)) from 0.7 mole of caproyl chloride, benzene and aluminum chloride[1]; the crude ketone solidified in ice. The 2,4-dinitrophenylhydrazone formed red needles which melted at 167.6–168.1° after one crystallization from ethanol–benzene (Evans, *J. Chem. Soc.*, 788 (1936), gives m. p. 168°). [i] Crystallized from aqueous methanol as white shining plates. *Anal.*[7] Calcd. for $C_{14}H_{21}NO$: C, 76.66; H, 9.65. Found: C, 76.96; H, 9.82. [j] Forms a gray powder from aqueous methanol whose melting point was not well reproducible. The sample sintered a few degrees below the melting point. *Anal.* Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75. Found: C, 69.29; H, 8.81. [k] Prepared in 89.5% yield (b. p. 217–219°) from 0.3 mole of *i*-caprophenone by Wolff–Kishner reduction (see first ref. in (*d*)). This compound had previously been prepared only by a Wurtz–Fittig reaction from benzyl bromide and isoamyl bromide (Schramm, *Ann.*, **218,** 390 (1883); Stenzl and Fichter, *Helv. Chim. Acta*, **17**, 669 (1934)). *i*-Caprophenone was prepared in 75% yield (b. p. 131.5–134° (11–12 mm.)) by a Friedel–Crafts reaction as described before.[1] The oxime of the isocaprophenone melted at 69.6–70.6° (lit. 71–72°), the semicarbazone at 142.2–142.8° (lit. 146°, 151°). The 2,4-dinitrophenylhydrazone formed dark red needles from alcohol–chloroform and melted at 178–179°. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66. Found: C, 60.41; H, 5.94. *i*-Caproyl chloride (b. p. 91.2–92.2° (144–145 mm.)) was obtained from 0.8 mole of *i*-caproic acid (Eastman Kodak Co. product, b. p. 198.1–198.5° (751 mm.)) and 0.96 mole of thionyl chloride in almost theroetical yield, m. p. amide 118.7–119.7°. [l] Crystallized first from ligroin and then from aqueous methanol, the monoacetamino derivative formed shining white plates. *Anal.* Calcd. for $C_{14}H_{21}NO$: C, 76.66; H, 9.65. Found: C, 76.76; H, 9.68. [m] Crystallized from aqueous ethanol as a white crystalline powder. *Anal.* Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75. Found: C, 69.76; H, 8.85. [n] See experimental part below.

pounds, as there existed a slight possibility of a rearrangement during the Friedel–Crafts reaction. The semicarbazone of *t*-butylacetophenone[12] forms transparent plates from alcohol, m. p. 218.4–219.6°. Mixed with the semicarbazone of phenyl neopentyl ketone it melts from 190–211°. The 2,4-dinitrophenylhydrazone of *t*-butylacetophenone, crystallized from alcohol–chloroform mixtures, forms hard, small, red plates from concentrated solutions and long orange needles from dilute solutions. The latter change to the former on contact with the solvent, m. p. 211.8–212.8°. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66. Found: C, 60.51; H, 5.78. The oxime of *t*-butylacetophenone forms white, fern-like needles from alcohol, which melt at 107.8–108.6° and also sublime near the melting point. Mixed melting point of this oxime with that prepared from phenyl neopentyl ketone shows a large depression. *Anal.* Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.22; H, 8.86.

1-Phenyl-3,3-dimethylbutane was prepared by Wolff–Kishner reduction[13] of the above ketone. The ketone (65

32, 6237 (1938), reports a m. p. of 219°. However, Baker, *J. Chem. Soc.*, 445 (1938), found a melting point of 231–232°.

(12) Prepared according to "Org. Syn.," Coll. Vol. II, p. 3 (1943).

(13) See first ref. in ref. *d* in Table I.

g.) was dissolved in 350 ml. of diethylene glycol and treated with 50 g. of potassium hydroxide and 40 ml. of 85% hydrazine hydrate for six hours (temp. up to 190°). On cooling the reaction mixture a yellow, crystalline solid (4.5 g.) separated and was filtered on a sintered glass funnel. The filtrate was worked up for the hydrocarbon as usual and afforded 49 g. (81.7%) of crude hydrocarbon distilling at 211–213.5° (761 mm.) (the bulk distilled at 212.5–213°). In another run on 52 g. of ketone a 72% yield of hydrocarbon, b. p. 210.8–211.2° (751 mm.), was obtained along with the yellow solid. The hydrocarbon was washed repeatedly with ice-cold sulfuric acid, water and carbonate and was distilled four times from sodium. The pure sample boiled at 211.6–212° at 750 mm., n^{20}_{D} 1.4826, n^{25}_{D} 1.4804, d^{25}_{25} 0.8482, d^{25}_{4} 0.8457. *Anal.* Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.10. The monoacetyl derivative forms characteristic shiny, white plates from aqueous methanol, m. p. 160.6–161.2°. *Anal.* Calcd. for $C_{14}H_{21}NO$: C, 76.66; H, 9.65. Found: C, 76.50; H, 9.69. The yellow solid was crystallized from alcohol-benzene and forms yellow needles, m. p. 148.4–149.2°. It has the correct analysis for the dihydrazone (dineopentyl phenyl ketazine). *Anal.* Calcd. for $C_{24}H_{32}N_2$: C, 82.70; H, 9.26. Found: C, 82.45; H, 9.54.

Preparation of 1-Phenyl-4,4-dimethylpentane

Benzalpinacolone was prepared from pinacolone and benzaldehyde by the method of Hill and Bramann, "Org. Syn.," Coll. Vol. I, 81 (1941).

Benzylpinacolone.—Hydrogenation of benzalpinacolone (m. p. 39–40°) at atmospheric pressure and room temperature in the presence of freshly prepared Raney nickel afforded benzylpinacolone as a colorless liquid boiling at 261.3° (746 mm.), n^{20}_{D} 1.4972, n^{25}_{D} 1.4949, in 75% average yield from 0.1 mole of unsaturated ketone.[14] *Anal.* Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.94; H, 9.45. The oxime of benzylpinacolone formed fine white needles from 50% aqueous ethanol melting at 97.5–98.1° (Hill and Bruce, ref. 14, p. 349, report a melting point of 95.5°). The semicarbazone formed small white needles from 50% ethanol melting at 157.2–157.7°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 68.00; H, 8.48. The 2,4-dinitrophenylhydrazone formed orange needles from ethanol-benzene melting at 179.4–180.3°. *Anal.* Calcd. for $C_{19}H_{21}N_4O_4$: C, 61.77; H, 5.73. Found: C, 61.50; H, 5.87. Attempted hydrogenation of a 1 mole sample and a 0.2 mole sample of benzalpinacolone (m. p. 39–40°) at atmospheric pressure and room temperature in the presence of Adams catalyst afforded a yellow inhomogeneous oil boiling at 266–278° (755 mm.). The material from the two runs was combined and separated into three fractions. The first fraction (b. p. 266–267° (755 mm.), n^{25}_{D} 1.5104) afforded a crude 2,4-dinitrophenylhydrazone melting at 173°; starting material was recovered from the two higher boiling fractions. The first fraction was resubjected to hydrogen at atmospheric pressure and room temperature in the presence of Raney nickel and yielded 54 g. of colorless material boiling at 260–262° (753 mm.), n^{25}_{D} 1.4947.

1-Phenyl-4,4-dimethylpentane (neoheptylbenzene) was prepared in yields ranging from 72 to 87% (b. p. 229–231°) from 0.2 to 0.3 mole of benzylpinacolone by the Huang-Minlon modification of the Wolff–Kishner reduction (see first ref. in ref. *d* of Table A); after removal of the water formed in the initial reaction, the reaction mixture was refluxed at 190° for five hours. The crude product was washed with successive portions of ice-cold concentrated sulfuric acid until the acid layer remained colorless, with water, aqueous sodium bicarbonate, water, dried over anhydrous potassium carbonate, and fractionated three times from metallic sodium. Three samples of neoheptylbenzene were prepared in this way for bromination studies. Two of the samples had been obtained from benzylpinacolone which was prepared by reduction of benzalpinacolone in the presence of Raney nickel; both of these samples were found to contain a rapidly brominated impurity. Attempted removal of the impurity by agitating the samples for forty-eight hours with aqueous potassium permanganate, followed by a second treatment with ice-cold concentrated sulfuric acid and refractionation from metallic sodium was unsuccessful. Treatment with 10 mole per cent. of bromine in the presence of iodine was also ineffective, and the samples were discarded. The third sample was prepared from the 54 g. of benzylpinacolone that had been obtained by hydrogenating benzalpinacolone in the presence of Adams catalyst and then in the presence of Raney nickel (see above). This third sample showed regular behavior in the bromination reactions; it had the following properties: b. p. 227.8–228.1° (759 mm.), n^{20}_{D} 1.4832, n^{25}_{D} 1.4809, d^{25}_{25} 0.8502, d^{25}_{4} 0.8477. *Anal.* Calcd. for $C_{13}H_{20}$: C, 88.57; H, 11.44. Found: C, 88.72; H, 11.32. The monoacetyl derivative formed white shining plates melting at 107.4–108.4° *Anal.* Calcd. for $C_{15}H_{23}NO$: C, 77.21; H, 9.93. Found: C, 77.03; H, 10.01. (Hill and Bruce, ref. 14, 351, who prepared 1-phenyl-4,4-dimethylpentane by reduction of benzylpinacolone with red phosphorus and hydriodic acid and zinc and sulfuric acid, report a boiling point of 115° (9 mm.), n^{20}_{D} 1.5281, 1.5267, d^{20}_{4} 0.9443. Francis (ref. *a* in Table A) questions the refractive index and density supplied by these authors and suggests the following revised calculated values: b. p. 233° (760 mm.), n^{20}_{D} 1.488, d^{20}_{4} 0.859.)

General Procedure

The general procedure and experimental conditions for the determination of the relative rates were similar to those previously described[1] with the exceptions noted in the case of *n*-hexyl-, *i*-hexyl- and neoheptylbenzene. All other hydrocarbons were studied in a solution which, after mixing of the reagents, was 0.2 *M* in hydrocarbon and 0.02 *M* in bromine (40 ml.). The solubilities of the three aforementioned compounds in 85% aqueous acetic acid are too low for the use of a 10-fold excess of hydrocarbon. *n*-Hexylbenzene and *i*-hexylbenzene were therefore studied at 8-fold excess (hydrocarbon 0.16 *M*, bromine 0.02 *M*), and neoheptylbenzene at a 6.5-fold excess (hydrocarbon 0.13 *M*, bromine 0.02 *M*). The hydrocarbons were dissolved in 35 or 39 ml. of solvent and 5 or 1 ml. of a bromine solution of appropriate strength was added. In order to provide a standard by which the 10% reaction times at a 10-fold excess could be calculated for these three compounds, *n*-amylbenzene was concurrently brominated at an 8- and 6.5-fold excess. The 10% reaction time at 10-fold excess for *n*-amylbenzene had previously been established. The 10% reaction times for *n*-hexylbenzene and *i*-hexylbenzene at an 8-fold excess were found to be 520 and 505 minutes, respectively; the 10% reaction time for neoheptylbenzene, at a 6.5-fold excess of hydrocarbon, is 570 minutes. The values for *n*-amylbenzene at an 8- and 6.5-fold excess are 480 and 520 minutes. From these values the figures recorded in Table I were obtained.

All 10% reaction times are rounded off to the nearest five minutes. An average of eight runs was carried out for each hydrocarbon. The values for *n*-hexyl-, *i*-hexyl- and neoheptylbenzene

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[14] Hill, Spear and Lachowicz, This Journal, **45**, 1560 (1923), and Hill and Bruce, *ibid.*, **52**, 348 (1930), report a boiling point of 247° (760 mm.) for this ketone.

may not be as accurate as those for the other compounds because an indirect method was used to establish the 10% reaction time. However, their order of reactivity is believed certainly to be correct.

Results and Discussion

Table I records the times for 10% reaction of bromine with twenty monoalkylbenzenes. The twelve monoalkylbenzenes previously studied are included in this table for comparison. All data are for brominations under identical conditions at 25° in 85% acetic acid 0.15 M in sodium acetate, using a 10-fold excess of hydrocarbon. In Table II relative rates of bromination, calculated from the data of Table I, are arranged in series of the type represented by Fig. 1.

TABLE I

TEN PER CENT. REACTION TIMES FOR BROMINATION OF MONOALKYLBENZENES

Alkylbenzene	Time in minutes for 10% reaction
Toluene	230
Ethylbenzene	330
n-Propylbenzene	415
i-Propylbenzene	570
n-Butylbenzene	390
i-Butylbenzene	620
s-Butylbenzene	710
t-Butylbenzene	1300
n-Amylbenzene	440
i-Amylbenzene	410
Neopentylbenzene	1110
2-Benzylbutane	505
2-Phenyl-3-methylbutane	(800)
2-Phenylpentane	690
3-Phenylpentane	840
t-Amylbenzene	1000
n-Hexylbenzene	475
i-Hexylbenzene	465
Neohexylbenzene	370
Neoheptylbenzene	480

TABLE II

RELATIVE RATES OF BROMINATION OF MONOALKYLBENZENES

R	Series I Ph-R	Series II $PhCH_2$-R	Series III Ph-$(CH_2)_2$-R	Series IV Ph-$(CH_2)_3$-R	Series V Ph-$(CH_2)_4$-R
Methyl	100	100	100	100	100
Ethyl	70	80	106	89	93
i-Propyl	40	53	101	84	
t-Butyl	18	30	112	81	

Two factors appear to influence the nuclear reactivities of monoalkylbenzenes in bromination reactions: (1) the number of hydrogen atoms in the side chain and their positions relative to the benzene ring, (2) the presence of a normal butyl chain linked to the ring.

The effect of the hydrogen atoms in the side chain on the reactivities of alkylbenzenes can best be evaluated in terms of series of the type represented by Fig. 1, although the same considerations are applicable to other compounds which are not members of these series. The reactivities depend primarily on the number of hydrogen atoms *alpha* to the benzene ring. However, if the number of *alpha* hydrogens is constant, the reactivities decrease as the number of *beta* hydrogens decreases. This is, for instance, the case for Series II (Table II) and also for the three compounds *i*-propylbenzene, *s*-butylbenzene and 3-phenylpentane ($PhCH(Me)_2 > PhCH(Me)(Et) > PhCH(Et)_2$; 100:80:68).[15] In the two series the number of *alpha* hydrogens is two and one, respectively, and the number of *beta* hydrogens decreases from three to none in the first, and from six to four in the second case. Second-order carbon–hydrogen hyperconjugation involving the *alpha* and *beta* C–H bonds has been suggested as a mechanism by which the effect of the *beta* hydrogens could be transmitted through a saturated methylene group.[1]

The new bromination data show that the four alkyl groups, methyl, ethyl, *i*-propyl, *t*-butyl, continue to affect the reactivity of the aromatic ring even when they are removed from the ring by more than one methylene group. Omitting Series III from consideration for a moment, it is observed that the compounds of Series IV (Table II) fall in the order *n*-butylbenzene > *n*-amylbenzene > *i*-hexylbenzene > neoheptylbenzene. The reactivities of these four compounds decrease with the number of hydrogen atoms on the *delta* carbon atom, of which there are three for *n*-butylbenzene and none for neoheptylbenzene, analogously to the way in which the reactivities of the compounds of Series I and II decrease with the number of *alpha* and *beta* hydrogens, respectively. In other words, the influence of the methyl, ethyl, *i*-propyl or *t*-butyl group is not completely damped even when a saturated three carbon atom chain is interposed between the alkyl group and the ring. The spacing of the relative rates is, however, considerably closer. By analogy with the structures proposed to account for the rates in Series II, second-order hyperconjugation structures of the type represented by Fig. 2 can tentatively be considered as an explanation for the apparent dependence of the

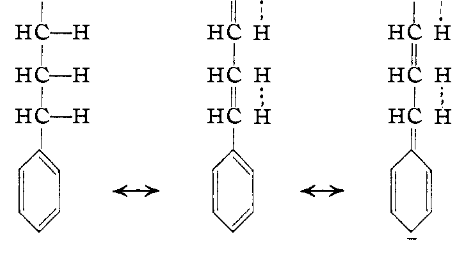

Fig. 2.—Hyperconjugation involving *delta* hydrogens.

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[15] Another example is presented by the series *i*-propylbenzene > *s*-butylbenzene > 2-phenyl-3-methylbutane; see ref. 1.

rates in Series IV on the number of *delta* hydrogens. The number of such structures decreases with the number of *delta* hydrogens.

In the above structures both the *alpha–beta* carbon–carbon bond and the *gamma–delta* carbon–carbon bond have acquired some double bond character in order to transmit the influence of the *delta* hydrogens to the ring.

Only two members of Series V, *n*-amylbenzene and *n*-hexylbenzene, have been investigated. *n*-Amylbenzene ($n = 4$, R = Me) is brominated faster than *n*-hexylbenzene ($n = 4$, R = Et). Thus the effect of varying the alkyl group is still transmitted to the benzene ring through a four carbon atom aliphatic chain. However, the strength of the effect diminishes as the number of carbons between the alkyl group and the ring is increased, as is evidenced by the progressively closer spacing of the relative rates in Series I to V (Table II).[16]

A comparison of *all* of the data shows that hyperconjugation of the *alpha* C–H bonds is more important than that of the *beta* bonds, that hyperconjugation of the *beta* bonds is more important than that of the *gamma*, etc., and that therefore the reactivities of monoalkylbenzene in electrophilic brominations depend primarily on the *alpha* C–H bonds and to progressively smaller extents on the number of *beta, gamma,* etc., linkages.[17,18] From the progressively closer spacing one can conclude that with a certain chain length the differences will presumably vanish.

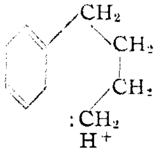

Fig. 3.—Chelative hyperconjugation.

The second factor influencing the reactivities of the alkylbenzenes is observed only in those compounds carrying a normal butyl chain or a substituted normal butyl chain. *n*-Butylbenzene is brominated faster than *n*-propylbenzene, in contradiction of the generalizations outlined above. This apparent anomaly of *n*-butylbenzene has been suggested to be due to additional resonance structures of the type shown in Fig. 3,[1] structures which may not contribute to alkylbenzenes with normal aliphatic chains of less than four carbon atoms; they represent chelation of the aliphatic chain with the *ortho* position of the benzene ring.[19] If such structures contribute to the reactivity of *n*-butylbenzene, they must also contribute to the reactivities of alkylbenzenes with substituted normal butyl chains. That such contributions do occur is supported by the following data. 2-Phenylpentane ($PhCH(CH_3)CH_2CH_2CH_3$) is brominated faster than 2-phenylbutane ($PhCH(CH_3)CH_2CH_3$) and 2-benzyl butane ($PhCH_2CH(CH_3)CH_2CH_3$) faster than *i*-butylbenzene ($PhCH_2CH(CH_3)_2$). In both cases the reverse would have been expected, but each of the more reactive compounds possesses a *n*-butyl chain. Moreover, in *i*-amylbenzene ($PhCH_2CH_2CH(CH_3)_2$) with six *delta* hydrogens and in neohexylbenzene ($PhCH_2CH_2C(CH_3)_3$) with nine *delta* hydrogens the probability for chelative hyperconjugation must be even greater than in *n*-butylbenzene, and an enhanced reactivity should ensue. *i*-Amylbenzene is brominated at a rate almost identical with *n*-propylbenzene, and neohexylbenzene is brominated faster than all other compounds studied with the exception of toluene and ethylbenzene.[20] These data, then, strongly support the suggestion that a *n*-butyl chain makes a contribution to the nucleophilic reactivity of the benzene ring in excess of the contribution which it would make if the electron releasing effect of the *delta* hydrogens could only be transmitted to the ring through the intervening four carbon atom chain.[21]

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(16) The closer spacing is in all probability not due to steric hindrance. Steric hindrance in the *ortho* positions must be a fairly constant factor in all series in which *n* is greater than zero.

(17) See, however, footnote 21.

(18) The relationship between the different bonds can be roughly expressed in the following manner. *One alpha* C–H bond exerts more influence than *three beta* C–H bonds, *one beta* more than *three gammas*, etc. This is evident from the order of reactivity of the *n*-alkylbenzenes (except *n*-butylbenzene which is discussed later, see footnote 21) or of such pairs as $PhCH_2CH_3 > PhCH(CH_3)_2$, $PhCH_2CH_2CH_3 > PhCH_2CH(CH_3)_2$, $Ph(CH_2)_3CH_2CH_3 > Ph(CH_2)_3CH(CH_3)_2$. *One alpha* bond also is usually more important than *four beta* bonds, *e. g.*, $PhCH_2CH(CH_3)_2 > PhCH(CH_3)CH_2CH_2CH_3$ and $PhCH(CH_3)CH_2CH_3$, $PhCH_2CH_2CH_3$ and $PhCH_2CH_2CH_2C(CH_3)_3 > PhCH(CH_3)_2$, $PhCH_2CH(CH_3)CH_2CH_3 > PhCH(CH_3)CH_2CH_2CH_3$, and *one beta* bond contributes more than *four gamma* bonds, *e. g.*, $PhCH_2CH(CH_3)_2 < PhCH_2CH_2CH_2C(CH_3)_3$. This relationship is probably a borderline case. The exceptions are 2-phenyl-3-methylbutane and 3-phenylpentane which are brominated faster than neopentylbenzene, but this may be due to the six *gamma* bonds in the faster compounds. Also, *i*-hexylbenzene is slightly faster than *n*-hexylbenzene. *One alpha* bond, however, is less important than *five beta* bonds ($PhCH(CH_3)_2 > PhCH_2CH(CH_3)_2$, $PhCH(CH_3)CH_2CH_3 > PhCH_2C(CH_3)_3$) and consequently less than six ($PhCH(CH_3)_2 > PhCH_2C(CH_3)_3$, also $PhCH_2CH_2CH(CH_3)_2 > PhCH_2CHCH_2C(CH_3)_3$ in the general case). These comparisons of *alpha*, *beta*, etc., C–H bonds do not show that the differences in relative rates become smaller with progress of the variable group away from the ring.

(19) For similar suggestions to account for the anomaly of the *n*-butyl group, see ref. 1.

(20) This high reactivity of neohexylbenzene cannot be due alone to the *alpha* and *beta* hydrogens (because it reacts faster than *n*-propylbenzene or *n*-butylbenzene), nor can the effect of the nine *delta* hydrogens be transmitted to the ring by the mechanism suggested by Figs. 2 and 4 because of the absence of *gamma* hydrogens. In contrast, neopentylbenzene, the lower homolog of neohexylbenzene, is brominated slower than any other compound studied with the exception of *t*-butylbenzene. This indicates, as stated above, that the effect of C–H bonds cannot be transmitted along the chain to the ring if there is a carbon atom with no hydrogens between the ring and the C–H bonds.

(21) In the presence of *delta* hydrogens the rules outlined in Footnote 18 can then be extended to the effect that *three delta* hydrogens are more important than *one gamma* hydrogen. But the *delta* hydrogens, by chelation, cannot compete with *alpha* or *beta* C–H bonds. One *beta* bond contributes more than nine *delta* bonds ($PhCH_2CH_3 > PhCH_2CH_2C(CH_3)_3$). The relationship expressed here and in Footnote 18 is obviously an oversimplification. However, the eighteen compounds with *alpha* hydrogens allow a comparison of 153 pairs of hydrocarbons. Of these only the following do not fit the relationship: (a) *i*-amylbenzene should be faster than *n*-butylbenzene (b) the exceptions noted in Footnote 18. It is also possible to assign arbitrary numerical values to the different types of bonds which express a similar relationship.

It must be a consequence of this chelation effect that the order of rates in Series III is quite unlike that in all other series. If the chelation effect were *absent*, the reactivities would be expected to be *n*-propylbenzene > *n*-butylbenzene > *i*-amylbenzene > neohexylbenzene, and such an order could be accounted for by hyperconjugation structures (Fig. 4) which are analogous to the structures proposed for the compounds of Series I, II and IV. If the chelation effect alone were *determinant*, the order of reactivities should be neohexylbenzene > *i*-amylbenzene > *n*-butylbenzene > *n*-propylbenzene, for this is the order in which the probability for chelation decreases. Neither order is experimentally observed, although only *i*-amylbenzene is out of line for the order based on chelation hyperconjugation (see Table II). The differences are so small that one can only speak of a trend in one direction, but it is noteworthy that, compared with all other series, the trend in Series III is definitely in the opposite direction. The closeness of the spacing is perhaps due to the operation of both effects with the chelation effect the stronger.

Unless a whole *delta* methyl group is required for chelation, the order of reactivity in Series IV is compatible with both the chelation hyperconjugation mechanism (Fig. 3) and the second-order hyperconjugation mechanism (Fig. 2), because both mechanisms require a decrease in reactivity with a decrease in the number of *delta* hydrogens. The data do not indicate if one or both mechanisms are operative. However, in Series V the number of *delta* hydrogens is constant, and therefore the differences in rate would seem to be due essentially to second-order hyperconjugation of the type represented by Figs. 2 and 4.

The resonance structures shown in Figs. 2–4 are admittedly unconventional. However, even if they have no physical significance, they present a consistent system of classification of the observed reactivities of alkylbenzenes. Beyond being a system of classification, the structures are assumed to indicate electronic adjustments that occur in the transition state; they may or may not contribute to the ground states of the molecules. They suggest that an alkyl chain, when attached to the highly polarizable benzene ring, may, if need arises, acquire enough double bond character to permit transmission of an effect, in much the same way in which such an effect can be transmitted through a system of conjugated double bonds.

Two factors complicate the interpretation of the experimental data. One is the smallness of some of the differences in rates, particularly in the higher series. However, even though the differences are in part very small, it is believed that they are real and that they merit the attempt of a critical interpretation. The second factor that complicates the interpretation of the data is the absence of reliable data on energies and entropies of activation. By analogy with many side-chain reactions and substitution reactions on the benzene ring, it would seem reasonable to assume that in the present reaction the differences in rates are determined largely by differences in energies of activation.[22] If this should not prove to be the case, the interpretation may have to be modified. The experimental conditions of the present work were such that a determination of the activation energies and entropies did not seem very promising.

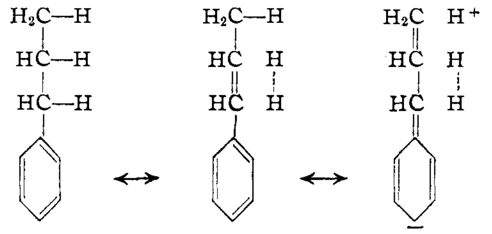

Fig. 4.—Hyperconjugation involving *gamma* hydrogens.

The best assurance that the data are amenable to interpretation in terms of the suggested resonance forms is their agreement with such an interpretation. Another explanation might prove equally consistent, perhaps one that treats the alkyl group as a unity instead of considering it to be made up of the group R and a number of methylene groups, or one that does not place the emphasis on the number and position of the C–H bonds. At present, however, the interpretation proposed here seems to present a workable hypothesis.

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Summary

The relative rates of bromination of twenty monoalkylbenzenes are: toluene 100, ethylbenzene 70, *n*-propylbenzene 55, *i*-propylbenzene 40, *n*-butylbenzene 59, *i*-butylbenzene 37, *s*-butylbenzene 32, *t*-butylbenzene 18, *n*-amylbenzene 52, *i*-amylbenzene 56, neopentylbenzene 21, 2-benzylbutane 46, 2-methyl-3-phenylbutane 29, 2-phenylpentane 33, 3-phenylpentane 27, *t*-amylbenzene 23, *n*-hexylbenzene 48, *i*-hexylbenzene 49, neohexylbenzene 62, neoheptylbenzene 48. The relative rates are correlated by means of hyperconjugation.

An enhanced relative rate of bromination is shown by those hydrocarbons having a simple or substituted *n*-butyl chain. This effect is interpreted in terms of an additional chelative hyperconjugation.

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[22] Williams and Hinshelwood, *J. Chem. Soc.*, 1079 (1934); Dresel and Hinshelwood, *ibid.*, 649 (1944); Watson, "Modern Theories of Organic Chemistry," second edition, Clarendon Press, Oxford, 1941, pp. 75–78; Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, pp. 118–123, 193–194. In the first order solvolysis of *p*-alkylbenzhydryl chlorides the relative rates are determined by the energies of activation (Hughes, Ingold and Taher, *J. Chem. Soc.*, 949 (1940)). However see Baker and Nathan, *ibid.*, 1840 (1935), and ref. 4; Davies, *ibid.*, 1865 (1938).