imidazolones (X) containing various substituents R in position 4 was studied. Depending on the nature of the substituent R, either the decarboxylated imidazolones (I, R = CH_3, C_2H_5, C_6H_5) or the corresponding acids (XI, R = C_2H_5, H) were obtained.

3. Friedel–Crafts acylations of 2-imidazolone, 4-methyl-2-imidazolone, and 4-ethyl-2-imidazolone were performed, and the obtained ketones (II) were hydrogenated to imidazolidone derivatives (IV). Thus a lower (IV, R = H) and a higher (IV, R = C_2H_5) homolog of desthiobiotin were synthesized.

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

No-Bond Resonance. The Competitive Bromination of Toluene and *t*-Butylbenzene

BY ERNST BERLINER AND FRANCES J. BONDHUS

Electrophilic substitution of *p*-alkyltoluenes takes place predominantly in the position *ortho* to the methyl group.[1,2,3] Le Fèvre,[2] who summarized the existing experimental data, realized that the course of substitution reactions on *p*-alkyltoluenes did not proceed according to the accepted order of the inductive effect, and ascribed the reversed order to steric repulsion due to increasing size of the alkyl groups. Baker and Nathan, however, interpreted the reactions on the basis of the now well known no-bond resonance effect without resorting to steric hindrance.[4,5,6] While there is little doubt as to the validity of the interpretation and the general usefulness of the concepts of no-bond resonance (hyperconjugation), it still seemed of interest to investigate the case of the *p*-alkyltoluenes. For example, the fact that *p*-*t*-butyltoluene is nitrated exclusively in the position *ortho* to the methyl group cannot be interpreted as indicating that the *t*-butyl group is completely incapable of increasing the electron density on the benzene ring. A preponderance of electron releasing capacity of the methyl group over that of the *t*-butyl group may be sufficient to cause the reaction to proceed entirely in one direction. Also, in spite of the electronic effects, some steric effect of the bulky *t*-butyl group cannot be completely discounted. Finally, in view of the strong *para* directing character of the *t*-butyl group and the fact that *t*-butylbenzene is more easily substituted than benzene, there must be some electron release from this group, which may or may not be the ordinary inductive effect, but cannot be due to first order hyperconjugation.

With this in mind the relative rates of substitution of toluene and *t*-butylbenzene by bromine were determined. Nuclear bromination is an electrophilic substitution reaction, and therefore belongs to those reactions for which an increased no-bond resonance effect should be expected. The usual comparison of the reactivity of two compounds toward substitution is the parallel bromination of hydrocarbons and the evaluation of the individual rate constants. By this method the rates of bromination of different alkylbenzenes have recently been determined by de la Mare and Robertson,[7] who interpreted their results in the light of hyperconjugation. Instead of employing the parallel method a simultaneous competitive bromination of the two hydrocarbons was chosen in the present investigation, because such a study lends itself to an immediate interpretation of the data, irrespective of the exact mechanism of the reaction, the nature of the active substituting agent, or accidental variations in temperature and other reaction conditions.[8] No matter what the conditions are, in a competitive bromination the hydrocarbon that furnishes the greater electron density at the point of attack will be brominated to the greater extent.

Toluene and *t*-butylbenzene were brominated simultaneously in 92% acetic acid using iodine as a catalyst, and the resulting mixture was analyzed for the amounts of bromotoluene and bromo-*t*-butylbenzene formed.

Experimental

The procedure followed was similar to the one used by Ingold and collaborators[8a,b] in the competitive nitration of benzene and toluene, but in the present case all of the brominated products could not be obtained in a single fraction. Two series of artificial mixtures, containing the same constituents as were obtained during the actual bromination, were prepared and their refractive indices and densities determined. One mixture consisted of *t*-butylbenzene and bromotoluene, the other of bromotoluene and bromo-*t*-butylbenzene. In the recovery of the brominated products the more volatile solvents were distilled, and the remainder was separated into two fractions. The amounts of brominated hydrocarbons in the two fractions were determined by measurements of the densities and refractive indices. The amounts of the three possible position isomers obtained from each hydrocarbon were not determined, and only the total brominated product was

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[1] Battegay and Haeffely, *Bull. Soc. Chim.*, **35**, 981 (1924).

[2] Le Fèvre, *J. Chem. Soc.*, 980 (1933); 1501 (1934).

[3] Brady and Day, *ibid.*, 114 (1934).

[4] Baker and Nathan, *ibid.*, 1844 (1935).

[5] Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, 1941, pp. 96-98.

[6] For a recent summary see Deasy, *Chem. Rev.*, **36**, 145 (1945).

[7] de la Mare and Robertson, *J. Chem. Soc.*, 279 (1943).

[8] (a) Ingold and Shaw, *ibid.*, 2918 (1927); (b) Ingold, Lapworth, Rothstein and Ward, *ibid.*, 1959 (1931); (c) Ingold and Smith, *ibid.*, 905 (1938); (d) Bird and Ingold, *ibid.*, p. 919; (e) Benford and Ingold, *ibid.*, p. 929.

taken into account. The bromo compounds that were used to prepare the artificial mixtures were prepared by the procedure used in the competitive brominations. The assumption is reasonable that the same amounts of isomers were formed in all cases. Polybromination or side chain bromination was not observed; if it occurred, the amount must have been very small. The formula of Ingold,[8b,c,9] by which the relative rates can be computed from the amounts of substituted products, was used to calculate the results.

Preparation of Materials. Toluene.—C. P. sulfur-free toluene was purified according to Fieser.[10] It was distilled three times through an electrically heated Widmer column, retaining that portion boiling at 109.3–110° (755.6 mm.) pressure. This material, enough for all runs, was stored over sodium in a brown bottle, $n^{25}\mathrm{D}$ 1.4930, $\mathrm{D}^{25}{}_{25}$ 0.8637.

t-**Butylbenzene.**—Of the several methods tried, a slight modification of the procedure of Huston, Fox and Binder[11] employing *t*-butyl alcohol, benzene and aluminum chloride was found to afford *t*-butylbenzene in the highest yields. In larger runs (three moles of alcohol) the yields (60–70%) claimed by these authors could not be duplicated without the inclusion of a one-hour heating period before decomposition of the reaction mixture; b. p. 165.5–166.5°, $n^{25}\mathrm{D}$ 1.4899, $\mathrm{D}^{25}{}_{25}$ 0.8650.

Glacial Acetic Acid.—Glacial acetic acid (99.8%) was frozen and allowed to melt slowly, decanting approximately the first 25% of the material to liquefy. The residue was distilled twice through an electrically heated Widmer column from 2% of its weight of potassium permanganate. The portion boiling at 117–118° (755.6 mm.) pressure, $n^{25}\mathrm{D}$ 1.3708, $\mathrm{D}^{25}{}_{25}$ 1.0511, was collected for use in the competition reactions. It was later found that the freezing of the acid was unnecessary. The 99.8% acid was distilled once from permanganate disregarding about one third in the fore- and after-runs.

Bromine and Iodine.—C. P. products were used without further purification.

Bromotoluene and Bromo-*t*-butylbenzene.—The individual brominations of toluene and *t*-butylbenzene were carried out under exactly those conditions employed in the competition reactions. One mole of bromine was used for one mole of hydrocarbon. The brominated hydrocarbons had the following physical constants: bromotoluene, $n^{25}\mathrm{D}$ 1.5512; $\mathrm{D}^{25}{}_{25}$ 1.4115; b. p. 79° (26 mm.); yield 53.5% and bromo-*t*-butylbenzene, $n^{25}\mathrm{D}$ 1.5309; $\mathrm{D}^{25}{}_{25}$ 1.2488; b. p. 117–118° (23 mm.); yield 35%.

Preparation of the Mixtures.—Two series of mixtures were prepared, one consisting of *t*-butylbenzene and bromotoluene, the other of bromotoluene and bromo-*t*-butylbenzene. The brominated hydrocarbons from the preceding brominations were used. The mixtures were prepared by weighing the two components on an analytical balance. Densities were measured in a 10-cc. pycnometer with a ground stopper, standardized with distilled water that had been boiled to expel all air. The pycnometer was placed in a thermostat maintained at 25 ± 0.01°. Refractive indices were determined with an Abbe refractometer at 25 ± 0.1°. Since all measurements were carried out at 25°, the values were not reduced to 4°. In the following tables the composition and physical constants of the mixtures are given.

TABLE I

DENSITIES AND REFRACTIVE INDICES OF *t*-BUTYLBENZENE-BROMOTOLUENE MIXTURES

Mole per cent. bromo-toluene	Moles bromo-toluene	Moles *t*-butyl-benzene	$n^{25}\mathrm{D}$	$\mathrm{D}^{25}{}_{25}$
0	....	Pure	1.4899	0.8650
3.14	0.0043	0.1326	1.4913	.8782
5.22	.0070	.1272	1.4923	.8872
8.70	.0110	.1154	1.4941	.9027
19.94	.0272	.1092	1.5001	.9543
24.62	.0340	.1041	1.5028	.9766
49.92	.0603	.0605	1.5173	1.1045
55.75	.0718	.0570	1.5210	1.1365
59.98	.0622	.0415	1.5238	1.1604

TABLE II

DENSITIES AND REFRACTIVE INDICES OF BROMOTOLUENE-BROMO-*t*-BUTYLBENZENE MIXTURES

Mole per cent bromo-toluene	Moles bromo-toluene	Moles bromo-*t*-butyl-benzene	$n^{25}\mathrm{D}$	$\mathrm{D}^{25}{}_{25}$
0	....	Pure	1.5309	1.2488
9.63	0.0067	0.0629	1.5321	1.2601
21.72	.0257	.0926	1.5340	1.2753
28.69	.0350	.0870	1.5351	1.2846
43.80	.0654	.0839	1.5380	1.3065
49.66	.0722	.0732	1.5391	1.3155
55.70	.0611	.0486	1.5402	1.3251
63.51	.0952	.0547	1.5419	1.3383
67.70	.0658	.0314	1.5429	1.3458
74.08	.1023	.0358	1.5440	1.3574
85.64	.1115	.0187	1.5471	1.3801
93.57	.1194	.0082	1.5496	1.3970
100	Pure	....	1.5512	1.4115

The values were plotted and the percentage compositions of the mixtures obtained from the actual runs were read directly from the curves.

Competitive Brominations.—The competitive reactions were carried out with 0.5 mole of each hydrocarbon to ensure sufficient material for analysis. Acetic acid was chosen as a solvent in order to obtain a fairly fast reaction and to eliminate side chain bromination.[12] In preliminary experiments on 0.5 mole of each hydrocarbon 80 and 90% acetic acid was used, but it was found that the brominated hydrocarbons produced are not soluble in 500 cc. of either mixture; two layers were formed during the reaction. As larger amounts of solvent were inconvenient to handle, 550 cc. of 92% acetic acid was employed and maintained a homogeneous mixture throughout the reaction.

For the analysis of the reaction mixture the products were fractionally distilled; the brominated hydrocarbons were collected in two fractions and the composition of each determined. In the lower boiling fraction (containing *t*-butylbenzene and bromotoluene) the values obtained from the refractive indices and those from the densities agreed within less than 0.5% (usually within 0.1%). In the higher boiling mixture (containing bromotoluene and bromo-*t*-butylbenzene) there was a divergence of a few per cent. between the two values (usually 3–5% but in some runs more), the higher values being obtained from the refractive indices. It was found that the divergence was due to the presence of small amounts of *t*-butylbenzene, which could not be separated by one distillation. The presence of *t*-butylbenzene in this higher boiling fraction obscured the results, elevating the value for the amount of bromo-*t*-butylbenzene formed and depressing the value for bromotoluene. In order to evaluate the error thus introduced, known mixtures were separated by the same procedure that was used for the separation of the actual reaction products. In a typical recovery run 0.32 mole of toluene, 0.44 mole of *t*-butylbenzene, 0.18 mole of bromotoluene, and 0.06 mole of bromo-*t*-butylbenzene were dissolved in 506 cc. of glacial acetic acid and the mixture separated as described below. The mixture was found to contain 0.156 mole of bromotoluene and 0.068 mole of bromo-*t*-butylbenzene. The recovery factor obtained from this run was applied to separations in which the frac-

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[9] See also, Davis and Farnum, THIS JOURNAL, 56, 883 (1934).

[10] Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Company, Boston, 1941, p. 364.

[11] Huston, Fox and Binder, *J. Org. Chem.*, 3, 251 (1938–1939).

[12] Bruner and Vorbrodt, *Chem. Zentr.*, 80, I, 1807 (1909).

tions were cut at 175°. When the fractions were cut at 177°, the recovery factor was somewhat smaller and was applied to those reactions where separation was made at the same temperature. Competitive bromination: in a typical run a mixture of 46.07 g. (0.5 mole) of toluene and 67.11 g. (0.5 mole) of *t*-butylbenzene was dissolved in 500 cc. of 92% (by volume) acetic acid and placed in an all glass, 2-liter, 3-necked, round-bottomed flask equipped with a reflux condenser, dropping funnel, and electrically driven glass stirrer. The apparatus was placed in a thermostat maintained at 25 ± 0.5° and protected from light. The stirrer was started and iodine (0.625 g., one-half mole per cent.) was added. One half of a mole of bromine dissolved in 50 cc. of 92% acetic acid was added to the solution through the dropping funnel over a period of thirty minutes. After the addition was complete, stirring was continued for eight and one-half hours. The mixture was then poured into 1 liter of cold water and stirred with sodium bisulfite to remove the unreacted bromine. The diluted mixture was extracted with 200-, 200- and 100-cc. portions of ether. The combined ethereal extracts were washed with two 200-cc. portions of 10% aqueous sodium bicarbonate, and two 200-cc. portions of 10% aqueous sodium carbonate. The alkaline washings were extracted with 100 cc. of ether, which was combined with the original ethereal solution; the total ether extract was then washed with distilled water and dried over anhydrous sodium carbonate. Separation was effected by means of a twenty-inch electrically heated column filled with glass helices. After removal of the ether and the toluene the temperature was raised and distillation continued until pure *t*-butylbenzene distilled. At that point the first fraction was collected until the temperature had risen to 175°. The column was allowed to drain; it was then removed and replaced by a small, all-glass vacuum distillation apparatus from which the total second fraction was distilled under the vacuum of the water-pump. There remained only a few drops of dark residue. The first fraction weighed 74.4 g. ($n^{25}\text{D}$ 1.5032, corresponding to 25.2 mole per cent. of bromotoluene; D^{25}_{25} 0.9802, corresponding to 25.3 mole per cent. of bromotoluene). The second fraction weighed 14.8 g. ($n^{25}\text{D}$ 1.5350, corresponding to 28 mole per cent. of bromotoluene; D^{25}_{25} 1.2778, corresponding to 24 mole per cent. of bromotoluene). The result, using the values obtained from the refractive indices, corresponds to 0.1518 mole of bromotoluene and 0.0532 mole of bromo-*t*-butylbenzene. The corrected values are 0.1715 mole of bromotoluene and 0.0469 mole of bromo-*t*-butylbenzene. Applying the equation of Ingold, *et al.*,[8b,c] $\left(k_x/k_y = \log \frac{x}{x_0} \Big/ \log \frac{y}{y_0}\right)$, where x and y are the final concentrations of the hydrocarbons and x_0 and y_0 are the initial concentrations) which takes into account the uneven decrease in reactants as the reaction progresses, the ratio of velocities is 4.27/1.

Discussion

The results of the individual runs are summarized in Table III. Columns I and II list the number of moles of bromotoluene and bromo-*t*-butylbenzene obtained in competitive bromination of one-half mole of each hydrocarbon. In column IV are reported the calculated ratios of the velocities of bromination of the two hydrocarbons. The figures show that under the conditions of the experiment toluene is brominated about four times faster than *t*-butylbenzene. At 45° the ratio is somewhat more in favor of *t*-butylbenzene, of which relatively more is brominated than at 25°; the total per cent. yield also increases appreciably (approx. 10%). In two runs carried out in 100% acetic acid the total amount of bromination was considerably less (34.6%), and sufficient material for exact density determinations was not obtained; but the results, calculated from the refractive indices only, indicate that the ratio is the same as with the 92% mixture.

TABLE III

THE COMPETITIVE BROMINATION OF ONE-HALF MOLE OF TOLUENE AND ONE-HALF MOLE OF *t*-BUTYLBENZENE WITH ONE-HALF MOLE OF BROMINE AT 25°

I Moles bromotoluene	II Moles bromo-*t*-butylbenzene	III Per cent. bromination	IV $\frac{k(\text{toluene})}{k(t\text{-butylbenzene})}$
0.1724[a]	0.0456[a]	43.6[a]	4.42[a]
.1971[a]	.0487[a]	49.2[a]	4.89[a]
.1747	.0522	45.4	3.90
.1715	.0469	43.7	4.27
.1533	.0447	39.6	3.91
.1746	.0537	45.7	3.78
.1841	.0504	46.9	4.32
			Av. 4.04
	At 45°		
0.2066	.0648	54.3	3.84
.2070	.0672	54.6	3.76
			Av. 3.80

[a] These two runs were carried out in 90% (400 cc.) and 92% (250 cc. only) acetic acid, respectively. A heterogeneous mixture resulted. They are not included in the average.

De la Mare and Robertson have measured the rates of bromination of individual alkylbenzenes in 85% acetic acid solution at 24°. They found that under the conditions of their experiments the ratio of the velocities of bromination of toluene and *t*-butylbenzene is 100 to 23, or 4.34, with which the present results are in good agreement. The fact that toluene is brominated about four times as fast as *t*-butylbenzene is consistent with the idea of no-bond resonance, and confirms the measurements of de la Mare and Robertson and their conclusions that hyperconjugation is responsible for the difference in rates. Any permanent inductive effect by the alkyl groups is overshadowed by the resonance effect.

Any steric effect that might be present cannot be evaluated from these figures, for the amounts of the individual isomers (*ortho–para* ratios) were not determined. Toluene affords more *ortho* substitution than *t*-butylbenzene,[13] and if the above figures are to mean that a methyl group on the benzene ring accelerates substitutions more than a similarly situated *t*-butyl group—which is believed to be true—the assumption has to be added that the total rate of substitution is not greatly influenced by the *ortho–para* ratio, that is, any bromine that cannot be accommodated in the *ortho* position will freely substitute in the *para* position without changing the total rate of bromination appreciably.[14] If this assumption holds,

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[13] For nitration see ref. 8b, and Craig, THIS JOURNAL, 57, 195 (1935).

[14] If the total rate does fall off somewhat because of steric hindrance of the ortho positions, the effect would probably not be very significant as compared to the resonance effect; see also ref. 7.

then the found ratio of the velocities expresses the relative ability for electron release (which may be a summation of the no-bond resonance effect and the inductive effect) of the two alkyl groups on the total benzene ring during a bromination reaction. The results are thus considered to lend support to the theory of alkyl conjugation with the benzene ring.

Summary

In 92% acetic acid toluene is brominated four times faster than *t*-butylbenzene. This is explained by no-bond resonance.

BRYN MAWR, PA. RECEIVED JUNE 27, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Dipole Moment of 1-Nitrobutane

BY JOHN G. MILLER AND HENRY S. ANGEL

The solution values of the dipole moments of the nitroparaffins are important reference standards for the estimation of the effect of resonance in nitro-compounds which cannot be studied in the gaseous state.[1] Inspection of the recorded solution measurements of the nitroparaffins reveals that only nitromethane has been studied in more than one laboratory, and its value is not a useful standard because of the low polarizability of the methyl group. The only values reported for higher nitroparaffins are those of Hunter and Partington[2] for nitroethane (3.19 *D*) and 1-nitrobutane (3.29 *D*), and that of Oesper reported by Smyth[3] for 2-nitropropane (3.40 *D*).

These higher nitroparaffins should have very nearly the same moments, to judge from the careful studies of the nitroparaffins in the gaseous state made by Smyth and his co-workers.[4] The wide variation in the values of these important reference compounds has led us to measure the moment of 1-nitrobutane, using benzene as solvent to conform with the previous work.

Experimental

Materials.—The 1-nitrobutane was prepared by the Commercial Solvents Corporation and was supplied us by courtesy of Dr. Glenn E. Ullyot of Smith, Kline and French Laboratories. It was repurified by distillation through an all-glass Widmer column. A 97-g. fraction boiling at 152.4 to 153.4° (cor.) was taken for the measurements. At 25° its density was 0.96825 g. per cc., and its refractive index, n_D 1.40840. The molar refractivity, R_D, calculated from these values is 26.29.

The benzene was c. p. material, dried over calcium chloride and freshly distilled over sodium before use. Its density and refractive index were 0.87391 and 1.49782 at 25°.

Apparatus.—The dielectric constant measurements were made with an apparatus and method described previously.[5] Seven frequencies were employed. The temperature used was 25 ± 0.01°.

Results and Discussion

Table I lists the solute mole fractions, N_2, dielectric constants, ϵ, and densities, d, of the solutions measured. Included in the table are two linear equations obtained from these data by the method of least squares, showing the dielectric constant and density as functions of the mole fraction of the solute. The errors listed in these equations are probable errors calculated by the method of Gauss.[6]

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA

N_2	ϵ	d
0.0015889	2.3021	0.87414
.0029209	2.3231	.87437
.0054479	2.3609	.....
.0100568	2.4353	.87507

$$\epsilon = 2.2768\ (\pm 0.0007) + 15.71\ (\pm 0.12)\ N_2$$

$$d = 0.87401\ (\pm 0.00004) + 0.1059\ (\pm 0.0067)\ N_2$$

The constants in these equations were used to calculate the polarization of the solute at infinite dilution, P_∞, by substitution in the Hedestrand formula.[7] The advantages of this method have been described by Halverstadt and Kumler.[8] The value of P_∞, obtained in this way, is 262.3 ± 1.8.

The Gauss calculation used here to show the precision of the measurements is a valuable adjunct to this method of estimating P_∞. In contrast to the analyses of precision usually accompanying such measurements, it provides a rigid, objective analysis and requires little additional work because it employs the normal equations already set up for the least squares calculations. By means of it, a proper weighting of the lower concentration values is obtained.

In the present case, the precision error in P_∞, ±1.8, is due entirely to the error, ±0.12, in the dielectric constant slope term. The density determinations, made at only three concentrations, contribute negligible error.

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(1) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 137.

(2) Hunter and Partington, *J. Chem. Soc.*, 309 (1933).

(3) Smyth, in Weissberger, "Physical Methods of Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1946, Chap. XX, p. 996.

(4) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).

(5) Miller, *ibid.*, **64**, 117 (1942).

(6) Whittaker and Robinson, "Calculus of Observations," 2nd ed., Blackie and Son, London, 1937, pp. 243–247.

(7) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(8) Halverstadt and Kumler, THIS JOURNAL, **64**, 2988 (1942).