rate determining ionization, plots of the logarithm of the first-order rate constant k in various solvents (either from the literature or here reported) against log k for t-butyl chloride are linear.

A set of values of the so-called ionizing power, Y, defined by the equation

$$\mathrm{Y} = \log k^{\mathrm{BuCl}} - \log k_0^{\mathrm{BuCl}}$$

(k^{BuCl} and $k_0{}^{\mathrm{BuCl}}$ being solvolysis rate-constants for t-butyl chloride at 25.0° in the given solvent and in 80% ethanol) has been set up for a number of solvents including water, methanol, ethanol, aqueous alcohols, formic acid and acetic acid. The solvolysis rate constants (varying sometimes by six orders of magnitude) are fitted by the equation

$$\log k = m\mathrm{Y} + \log k_0$$

with a mean probable error of less than 0.05 in the cases of t-butyl bromide, neopentyl bromide, α-methylneopentyl p-bromobenzenesulfonate, α-methylallyl chloride, α-phenylethyl chloride and benzhydryl chloride.

The observed linear relationships, interpreted on the basis of the Brönsted equation, lead to the equation

$$\log \frac{f_{\mathrm{A}}}{f_{\mathrm{A}}^{\ddagger}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \log \frac{f_{\mathrm{B}}}{f_{\mathrm{B}}^{\ddagger}} + \text{constant}$$

for the relationship among the pertinent activity coefficients ($f_{\mathrm{A}}, f_{\mathrm{A}}^{\ddagger}$, *etc.*) for any two compounds A and B. It is postulated that linear logarithmic relationships among ratios of activity coefficients of this type may be quite general.

The solvolysis of t-butyl chloride is discussed in terms of the Brönsted equation. It is shown that, to a good approximation, $\log f_{\mathrm{BuCl}}^{\ddagger}$ varies linearly with $\log f_{\mathrm{BuCl}}$ in the partly aqueous solvents and that in these solvents the variation in k is due largely to changes in f_{BuCl}. On the other hand, in the more poorly ionizing solvents changes in k are attributable mainly to changes in $f_{\mathrm{BuCl}}^{\ddagger}$.

The reported method of correlating unimolecular type solvolysis rates is useful in elucidating the nature of the solvolysis of materials the rates of which depend markedly on the nucleophilic character of the solvent. For isopropyl p-bromobenzenesulfonate the rates of solvolysis in acetic acid and acetic acid–acetic anhydride mixtures furnish estimates of unimolecular solvolysis rates in ethanol, methanol and aqueous ethanol. The actual solvolysis rates are considerably larger in the latter solvents, the fractions of unimolecular solvolysis being low.

LOS ANGELES 24, CALIFORNIA RECEIVED AUGUST 15, 1947

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

Hyperconjugation. II. The Competitive Bromination of Benzene and *t*-Butylbenzene

BY ERNST BERLINER AND FRANCES J. BONDHUS

When benzene and t-butylbenzene in an equimolecular mixture in 92% acetic acid are allowed to compete for an insufficient amount of bromine, the corresponding brominated hydrocarbons are formed in proportions which show that the ratio of the rates of bromination at 25° is about 115:1 in favor of t-butylbenzene. At 45° the ratio is about 72:1. Therefore the bromination of benzene requires a higher energy of activation than the bromination of t-butylbenzene.[1] Since under the same conditions toluene is brominated about four times faster than t-butylbenzene,[2,3] the rate of bromination of toluene appears to be about 465 times faster than that of benzene. Values for the individual rates of chlorination of toluene and benzene fix the ratio at about 345,[3,4] whereas in nitration with acetyl nitrate toluene reacts twenty-three times faster than benzene.[5]

The difference in the rates of bromination of toluene and t-butylbenzene was explained by no-bond resonance of the Baker–Nathan type,[2,3,6] which involves carbon–hydrogen bonds, but the much greater difference between t-butylbenzene and benzene clearly cannot be accounted for by such resonance, since no α-hydrogen atoms are available for conjugation.[7] On the other hand, it would be hard to see how the inductive effect, which, on the basis of the Baker–Nathan theory, should be operative in the absence of hydrogen atoms, could alone account for the great activation and strong *ortho–para* directive influence of the t-butyl group, particularly since inductive effects of alkyl groups are conceded to operate through a rather feeble relay mechanism. The definitions that make the Baker–Nathan type of resonance

---

[1] The bromination of different aromatic compounds is probably another case in which the differences in rate are primarily due to differences in the E term of the Arrhenius equation (Scheffer and Blanksma, *Rec. trav. chim.*, **46**, 522 (1928); Bradfield and Jones, *J. Chem. Soc.*, 1006 (1928)); *i. e.*, the relationship $(\log k_1/k_2)_{T_1} = T_2/T_1 (\log k_1/k_2)_{T_2}$ should hold. In the competitive bromination of toluene and t-butylbenzene the calculated ratio at 45° is 3.70 (found, 3.80); in the present bromination the agreement is less satisfactory (calculated ratio at 45°: 85.7, found: 71.5). This may be due to irregularities on account of the greater difference in rate.

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

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

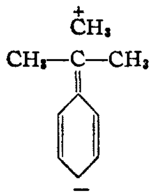
(4) This ratio is for 80% acetic acid; the ratio of the rate of chlorination of t-butylbenzene and benzene is 110.

(5) Ingold, Lapworth, Rothstein and Ward, *J. Chem. Soc.*, 1959 (1931).

(6) Baker and Nathan, *ibid.*, 1840 (1935).

(7) Baker, *ibid.*, 1150 (1939).

dependent upon the number of hydrogen atoms available for conjugation are, however, not inherent in the quantum mechanical treatment of the problem.[8] According to this approach any three single bonds can take part in hyperconjugation, if they are linked to a carbon atom which is conjugated with a multiple link. It has been more or less assumed that the carbon–hydrogen bond is capable of contributing more to hyperconjugation than an equally situated carbon–carbon bond, an idea that is supported by a fairly large number of reaction rates and equilibrium constants that have been studied by Baker and his school.[9] Although this concept seems thus fairly well established experimentally, it has also been stated that "...every carbon–carbon single bond can act as hyperconjugation donor wherever this is needed, without appreciable cost."[10] In view of the unexpectedly large contrast in the rates of bromination of benzene and *t*-butylbenzene, the *t*-butyl group must be considered to release electrons and partake in resonance through the contributions of structures of the type



The order of electron release of alkyl groups by this mechanism is identical with the order of the inductive effect, *i. e.*, *t*-butyl > *i*-propyl > ethyl > methyl,[11] and the reverse of the order of the hyperconjugation effect involving hydrogen atoms only (Baker–Nathan effect).

Reinterpretation of the inductive effect of alkyl groups as a resonance effect allows all observed electron release by these groups to be treated from a common basis. This might seem particularly advantageous in that the origin of the inductive effect has always been obscure.[12] It does not, *a priori*, answer the vexing question: why should there be two differing orders of electron release by alkyl groups, *i. e.*, why does carbon–hydrogen hyperconjugation contribute more in some cases, whereas in others resonance of carbon–carbon links takes precedence?[13] Thus, in the bromination of alkylbenzenes hyperconjugation appears to be predominant in toluene, but it must still be appreciable in *t*-butylbenzene, where only carbon–carbon hyperconjugation is possible.

Measurements of physical constants, on the whole, seem to reveal increasing contributions from resonance with increasing number of carbon–carbon links available for hyperconjugation, whereas rates and equilibrium constants indicate a greater tendency for carbon–hydrogen hyperconjugation. It is true that in many of the reactions that have been studied the differences in rate or equilibrium constants are very small, and in the majority of the cases the sequence of the alkyl groups is far from clean or regular, but enough well spaced series have been obtained to establish the Baker–Nathan order for reactions and equilibria with a good deal of certainty, even though only as a trend.[14,15]

Table I summarizes some of the pertinent data referring to both physical constants and chemical reactions. The new figures for the resonance energies of alkylbenzenes deserve some comment. It is generally agreed that small differences in experimental resonance energies must not be relied upon too strongly, since the values are obtained as small differences of two large figures, both subject to experimental errors.[16] The heats of combustion, on which the present data are based, have been determined on extremely pure samples by one reliable group at the National Bureau of Standards.[17] If one is justified in using thermochemical data for the calculation of resonance energies, the present set of data is surely reliable. The alkylbenzenes thus show resonance energies that increase with the amount of branching, *i. e.*, they follow the order produced by hyperconjugation of carbon–carbon bonds (line 1).[18,19,19a] In lines 2 and 3 of Table I are listed the dipole moments and molecular exaltations of the alkylben-

---

[8] Mulliken, *J. Chem. Phys.*, **7**, 339, 356 (1939).

[9] See Baker and Hemming, *J. Chem. Soc.*, 191 (1942), for the preceding references.

[10] Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941).

[11] Resonance structures of the type R+ —Ar place the alkylbenzenes in the same order.

[12] Ingold, *Chem. Rev.*, **15**, 225 (1934).

[13] The problem of the order of the "inductive" effect *versus* the order of the resonance effect has been treated by Baker and his co-workers in terms of the relative energy levels (ref. 7 and 9, and *Trans. Faraday Soc.*, **37**, 632 (1941)) by which numerical values are assigned to the two effects. According to the present presentation it would not seem justified to assign a zero value to the resonance effect of the *t*-butyl group.

[14] For a general survey see: Deasy, *Chem. Rev.*, **36**, 145 (1945).

[15] The rates of chlorination of different alkyl phenyl ethers (Jones, *J. Chem. Soc.*, 1831 (1935)), the relative directive influence of alkoxyl groups (Robinson and Smith, *ibid.*, 392 (1926), 2647 (1927)), and of alkyl benzoates (Zaki, *ibid.*, 983 (1928)), that have often been cited in support of the pure order of the inductive effect, can actually be accounted for by a Baker–Nathan order. Since conjugation between the alkyl groups and the benzene ring is not possible through the intervening oxygen atom the increase in electron density on the ring will ultimately depend on the partial ionic bond character of the alkyl–oxygen bond, which in turn will depend on the stability of the alkyl carbonium ion (or something approaching it); see footnote 18.

[16] Wheland, "The Theory of Resonance," John Wiley & Sons, Inc., New York, N. Y., 1944, p. 63.

[17] Prosen, Johnson and Rossini, *J. Research Natl. Bur. Standards*, **36**, 455 (1946). The resonance energies are calculated from Pauling's bond energy values, ref. 16, p. 75.

[18] The figures, *inter alia*, also suggest that any effect based on the order *t-butyl* > methyl cannot be entirely due to induction, but must be, at least in part, a resonance effect, because no stabilization is assumed to accompany the inductive effect. However, the inductive effect of *all* groups is due to partial ionic bond character, and is thus a resonance effect.

[19] F. J. Bondhus, Ph.D. Dissertation, 1947, Bryn Mawr College, Bryn Mawr, Pa.

[19a] It might be argued that the bond energy values are not accurate enough to warrant an interpretation of the small differences; it is felt, however, that the observed *relative order* is significant. The calculations of Wheland and Pinkston (*J. Chem. Phys.*, **12**, 69 (1944)) refer only to second order hyperconjugation.

TABLE I

		Hydrogen	Methyl	Ethyl	*i*-Propyl	*t*-Butyl
1	Resonance energies of alkylbenzenes (kcal.)	39.5	42.4	42.3	43.5	44.9
2	Dipole moments of alkylbenzenes[a]	0	0.37	0.58	0.65	0.70
3	Molecular exaltations[b] *EM*D at 20°	−0.124	0.169	0.221	0.262	0.207
	*EM*D at 25°	−0.106	0.187	0.240	0.285	0.231
4	$k \times 10^4$ for R. of *p*-alkylbenzyl bromides with pyridine[6]	4.817[c]	7.983	6.733	6.500	6.467
5	First order solvolysis of *p*-alkylbenzhydryl chlorides[28] (a) alcoholysis	1	23.4	22.6	20	18.6
	(b) hydrolysis	1	21.4	17.3	13.8	10.9
6	10^3K for cyanohydrin reaction of *p*-alkylbenzaldehydes[9]	4.47	8.98	8.18	8.04	7.49
7	Chlorination of alkylbenzenes[3,4]	0.29	100	84	51	32
8	Bromination of alkylbenzenes[3]	...	100	76	44	23
9	Competitive bromination of alkylbenzenes	0.215	100	....	....	24.7
10	Per cent. dissociation of *p*-alkylhexaphenylethanes[f]	2.1[d]	16[e]	17[f]	26	33 (*s*-butyl)

[a] Baker and Groves, *J. Chem. Soc.*, 1144 (1939). [b] The molecular refractivities were taken from "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, American Petroleum Institute, Research Project 44, Washington, D. C., Table 5b (June 30, 1945; May 31, 1947) and Table 14b (January 31, 1946; May 31, 1947). [c] Baker and Nathan, *J. Chem. Soc.*, 519 (1935). [d] Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937). This degree of dissociation was determined in a 0.1 m. solution; in the other cases the molarity was 0.08. [e] Marvel, Rieger and Mueller, *ibid.*, **61**, 2769 (1939). [f] Marvel, Mueller, Himel and Kaplan, *ibid.*, **61**, 2771 (1939). (See footnote 36.)

zenes, which parallel the resonance energies, except for the exaltation of *t*-butylbenzene, which shows a reversal. Exaltation data have been used by Mulliken,[8] and by Hurdis and Smyth[20] to detect the presence of hyperconjugation. Data on the absorption spectra are only available for some alkylcyclohexenes,[21] and these do not demonstrate any differences.[22] No differences are shown in the heats of hydrogenations of alkylolefins,[23] but any differences would be expected to be smaller in the olefins than in the alkylbenzenes. Attention is also directed to the increasing stability of the free radicals formed from *p*-alkylhexaphenylethanes (line 10). The remainder of Table I records reaction rates and one equilibrium constant that show the opposite order (*i. e.*, the Baker–Nathan order) of the effect of alkyl groups.

Resonance involving the carbon–carbon bond was used at an early date by Wheland to account for the stability of free radicals formed from secondary or tertiary dialkyltetraarylethanes,[24] and later by Lewis and Kasha for the phosphorescence of di-isopropyl ketone.[25] It has recently been employed to explain the decreasing dipole moments of branched aliphatic amines.[26] The very small difference in dipole moments of *i*-propyl and *t*-butyl chloride as compared with the larger difference between methyl and ethyl chloride has been discussed by Smyth,[27] and can similarly be explained by the postulation of structures of the type $^{-}CH_3(CH_3)_2C{=}Cl^{+}$. The decreasing strengths of aliphatic branched acids can be accounted for in a like manner, as can other data, whenever alkyl groups are situated next to an atom having unshared electrons available for the formation of another bond.[19]

Why two opposing orders, based on the same effect, should be operative is at present not obvious. Since the data indicate that carbon–carbon hyperconjugation contributes more to the ground state of the resting molecule than carbon–hydrogen hyperconjugation, one might be justified in looking for deviations from the order required by carbon–carbon hyperconjugation in the energy and configurational requirements of the transition state.[28] Of the factors that might conceivably influence the stability of the transition state and be responsible for the inverted order of electron release by alkyl groups, the following might be of importance. Hydrogen is more electropositive than carbon on the electronegativity scale,[29] and a resonance structure that places a negative charge on the more electronegative atom (carbon) should, on this basis, be favored over other possible structures.[30a] Such an effect should be influenced by the solvent and the extent of solvation, and might be of considerable importance in reactions such as these, which have been carried out in strongly polar solvents or in the presence of acids and bases. It is perhaps significant in this connection that, whereas toluene does not exchange its hydrogens in neutral medium,[28] a slow deuterium exchange is reported to take place in alkaline solution.[31] This does not

---

(20) Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

(21) Bateman and Koch, *J. Chem. Soc.*, 600 (1944).

(22) In the case of the nitroalkylbenzenes there is a slight increase of the maximum at 2650 in the expected order, *p*-methyl < *p*-*i*-propyl < *p*-*t*-butylnitrobenzene, and also in the order *m*-methyl < *m*-*t*-butylnitrobenzene. Brown and Reagan, THIS JOURNAL, **69**, 1032 (1947).

(23) Conant and Kistiakowsky, *Chem. Rev.*, **20**, 181 (1937).

(24) Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(25) Lewis and Kasha, THIS JOURNAL, **66**, 2100 (1944).

(26) Rogers, *ibid.*, **69**, 457 (1947).

(27) Smyth, *ibid.*, **63**, 57 (1941).

(28) The problem of the transition states for these reactions has also been discussed by Hughes, Ingold and Taher, *J. Chem. Soc.*, 949 (1940).

(29) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 60, 64.

(30) Remick, "Electronic Interpretations of Organic Reactions," John Wiley and Sons, New York, N. Y., 1943, p. (a) 463, (b) 462.

(31) Miklukhin and Brodskii, *Compt. Rend. Acad. Sci. U. R. S. S.*, **53**, 437 (1946). (*Chem. Abs.*, **41**, 2700 (1947.) The exchange probably takes place in the side chain rather than the nucleus, because *p*-nitrotoluene is reported to exchange much more readily than toluene.

mean that hyperconjugation implies an ionization, as has been suggested[32] and repudiated,[28] but resonance will be an important factor leading to dissociation.[33] Carbon–hydrogen hyperconjugation should also be favored by the greater polarizability of the carbon–hydrogen bond, than that of the carbon–carbon bond,[34] a factor that should be important for the transition state of reactions depending on accession of electrons to the seat of reaction (Ingold's time-variable electromeric polarizability).[30b] The above factors might contribute to the Baker–Nathan order, but unlike the bond polarizabilities and electronegativities, the bond energy is smaller for the carbon–carbon bond than for the carbon–hydrogen bond.[35] If bond energies influence the stability of structures contributing to a resonance hybrid, then carbon–carbon hyperconjugation should represent an energetically preferred state. Since bond energies, however, refer to symmetrical cleavage of the bonds, it might seem plausible that reactions involving free radicals should show an order depending on carbon–carbon hyperconjugation. Such resonance would then account for the observed degree of dissociation of *p*-alkylhexaphenylethanes into free radicals,[36] and the stability of alkyldiaryl free radicals, which according to Conant increases with increasing amount of branching of the alkyl group.[37] That this increase in stability is a result of hyperconjugation is indicated by some calculations of Wheland.[24]

Experimental

Preparation of Materials

Benzene.—Thiophene-free benzene was distilled once from sodium through a 20-inch, electrically heated column filled with glass helices. The fraction boiling at 79.8° (755.7 mm.), m. p. 5.3–5.4°, d^{25}_{25} 0.8754, n^{25}_{D} 1.4972, was collected and stored over sodium in an amber bottle for use in the competitive brominations.

***t*-Butylbenzene.**—*t*-Butylbenzene was prepared as previously described.[2] Material boiling at 165–166° (755 mm.), d^{25}_{25} 0.8645, n^{25}_{D} 1.4898, was used in the competition reactions.

Glacial Acetic Acid.—J. T. Baker C.P. analyzed glacial acetic acid was used without further purification.

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

Bromobenzene and Bromo-*t*-butylbenzene.—Individual brominations of benzene and *t*-butylbenzene were conducted under conditions duplicating those used in the competition reactions. In the bromination of benzene no evidence of the formation of dibromobenzene was obtained. The product boiled at 155° (755 mm.), n^{25}_{D} 1.5557. The pure bromo-*t*-butylbenzene obtained upon bromination of *t*-butylbenzene had the following physical constants: b. p. 226° (752.5 mm.), d^{25}_{25} 1.2493, n^{25}_{D} 1.5309. These materials were prepared for use in analyzing the mixtures obtained from the competitive brominations.

Competitive Brominations

The competitive brominations of benzene and *t*-butylbenzene were conducted as described in Part I. Bromination of a homogeneous mixture of 0.5 mole of each hydrocarbon dissolved in 500 cc. of 92% aqueous acetic acid with 0.5 mole of bromine dissolved in 50 cc. of 92% aqueous acetic acid was carried out for twenty-four hours at 25 ±0.5° and for eight hours at 45 ±0.5° using one-half mole per cent. of iodine as a catalyst. The results of the individual runs are recorded in Table II.

TABLE II

Run	Moles bromobenzene formed	Moles bromo-*t*-butylbenzene formed	k_1/k_2
1 at 25°	0.0021	0.1919	114.9
2 at 25°	.0020	.1886	118.1
3 at 25°	.0020	.1832	113.9
			Av. 115.6
4 at 45°	.0034	.1927	71.4
5 at 45°	.0035	.1977	71.6
			Av. 71.5

Analysis of the reaction mixtures by the procedure employed in Part I was supplemented by an analytical determination of bromine. This seemed particularly desirable because the amount of bromobenzene in the *t*-butylbenzene fraction was very small, and refractive indices could not be used for its detection. The products of the reaction were separated into a bromobenzene–*t*-butylbenzene mixture and a *t*-butylbenzene-bromo-*t*-butylbenzene mixture by fractional distillation. Determination of the density of each fraction supplied directly the weight per cent. of brominated hydrocarbon in each, by comparison with weight per cent.-density curves derived from artificial mixtures of the desired components. Data from which the weight per cent.-density curve of bromo-benzene-*t*-butylbenzene mixtures was plotted are recorded in Table III.

TABLE III

DENSITIES OF BROMOBENZENE-*t*-BUTYLBENZENE MIXTURES

Weight per cent. bromobenzene	d^{25}_{25}
0	0.8645
2.75	.8747
3.61	.8781
4.41	.8812
4.95	.8834

The density–weight per cent. relationship of *t*-butylbenzene–bromo-*t*-butylbenzene mixtures is linear (per cent. bromo-*t*-butylbenzene = $180.2D - 125.12$) in the range 98–100% bromo-*t*-butylbenzene, the range required for analysis of the high boiling fraction obtained from the competition reactions.

The bromine content of each fraction was determined by subjecting weighed samples to Wurtz type reactions and titrating the bromide ion formed by the Volhard method.[38] The latter determinations checked the density determinations of brominated hydrocarbons within 0.2%.

In a control run containing 0.33 g. (0.0021 mole) of bromobenzene 0.32 g. (0.0020 mole, 97%) was recovered. The agreement was considered satisfactory, and no corrections were applied to the final figures.

In a representative run a mixture of 39.06 g. (0.5 mole) of benzene, 67.11 g. (0.5 mole) of *t*-butylbenzene, 500 cc. of 92% aqueous acetic acid and 0.625 g. of iodine was

---

(32) Robinson, *Chem. & Ind.*, **55**, 962 (1936).

(33) The solvent composition also has an appreciable effect on the spacing of the different rate constants in the first order solvolysis of the *p*-alkylbenzhydryl chlorides; see Table I, line 5.

(34) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Reinhold Publ. Corp., New York, N. Y., 1931, p. 152; see also Remick, ref. 30, p. 79.

(35) Pauling, ref. 29, p. 53.

(36) As long as the similar effect of groups in the *meta* position remains unexplained the data on the degree of dissociation have to be treated with reserve. See also Wheland, ref. 16, p. 194.

(37) Conant, *J. Chem. Phys.*, **1**, 427 (1933).

(38) For similar determinations see Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937), and the references given there.

placed in a 1-liter, 3-necked, round-bottomed flask equipped with a reflux condenser, dropping funnel, and electrically driven glass stirrer and brought to constant temperature in a thermostat maintained at 25 ± 0.5°. One-half mole of bromine dissolved in 50 cc. of aqueous acetic acid was added to the solution through the dropping funnel, with constant stirring, over a period of one hour. Stirring at constant temperature was continued for twenty-three hours after completion of the addition of bromine. The reaction mixture was then poured into cold water and stirred with bisulfite to remove the unreacted bromine. The diluted mixture was divided into two portions. Each portion was extracted with two 200-cc. portions of ether. The ethereal extract was washed with aqueous sodium carbonate until all evolution of carbon dioxide had ceased. The alkaline washings were combined and extracted with 100 cc. of ether. The combined ethereal extracts were dried over anhydrous sodium carbonate for distillation. The ether and unreacted benzene were removed and discarded. Separation of the residue was effected by means of a twenty-inch electrically heated column filled with glass helices. The first fraction, containing bromobenzene and *t*-butylbenzene, distilled at 150–170°, d^{25}_{25} 0.8678, amount 37.4 g. The column was allowed to drain and was replaced by a small distillation outfit through which the entire residue, consisting of *t*-butylbenzene and bromo-*t*-butylbenzene, was distilled. This second fraction contained 41.2 g. of material, d^{25}_{25} 1.2453.

The density of the first fraction corresponds to 0.88% bromobenzene (0.0021 mole). The density of the second fraction corresponds to 99.28% bromo-*t*-butylbenzene (0.1919 mole).

A 4.3390 g. (5 cc.) sample of fraction I was dissolved in 40 cc. of ether and allowed to stand in contact with 1 g. of sodium wire overnight at room temperature. The sodium which had not reacted in twelve hours was destroyed with ethanol. The sodium bromide formed was extracted with water. The aqueous solution was diluted to 50 cc., of which 10-cc. portions were treated with 5 cc. of 0.1 *N* silver nitrate solution. The excess silver nitrate was titrated with 8.65 cc. of 0.0522 *N* potassium thiocyanate. This value corresponds to 0.0021 mole of bromobenzene in fraction I.

A 1.2453 g. (1-cc.) sample of fraction II was dissolved in 40 cc. of benzene and refluxed with 2 g. of sodium, cut into small pieces, for five hours. The aqueous extract of the sodium bromide formed was diluted to 100 cc.; 10-cc. portions were treated with 10 cc. of 0.1 *N* silver nitrate. The excess silver nitrate was titrated with 8.05 cc. of 0.0522 *N* potassium thiocyanate. The titration value corresponds to 0.1918 mole of bromo-*t*-butylbenzene in fraction II.

Applying the equation of Ingold, *et al.*,[5,39] $k_x/k_y = (\log x/x_0)/(\log y/y_0)$, where x and y represent the final concentrations of *t*-butylbenzene and benzene and x_0 and y_0 the initial concentrations, the ratio of velocities is 114.9/1.

Acknowledgment.—We gratefully acknowledge the assistance afforded by a grant from the Penrose Fund of the American Philosophical Society.

Summary

1. *t*-Butylbenzene is brominated about 115 times faster than benzene at 25°. This is explained by hyperconjugation involving carbon–carbon bonds.

2. It is pointed out that the so-called inductive effect of alkyl groups may be explained by hyperconjugation, and it is suggested that this may explain the entire effect. The factors that influence the operation of the effect are discussed.

---

[39] Ingold and Smith, *J. Chem. Soc.*, 905 (1938).

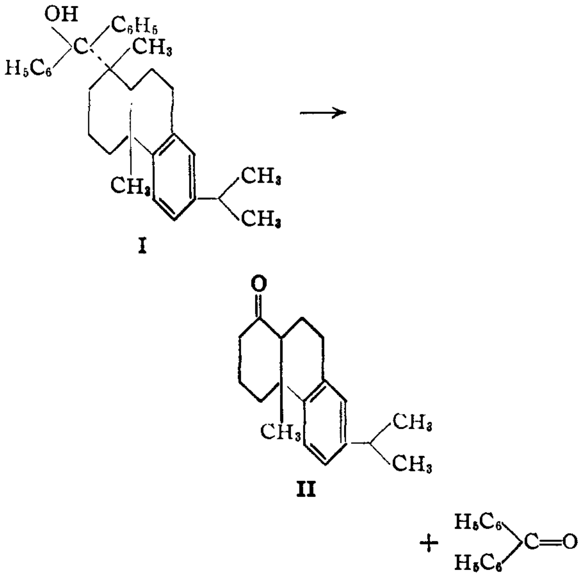
BRYN MAWR, PA. RECEIVED AUGUST 8, 1947

[CONTRIBUTION FROM RIDBO LABORATORIES, INC.]

Studies on Resin Acids.[1] II. The Oxidation of Diphenyl-*t*-dehydroabietinol. A Postulated Mechanism

BY HAROLD H. ZEISS

The oxidation of tertiary alcohols is not a reaction generally employed in the laboratory principally because of product complexity and low yields. In the course of our study of the resin acids the previously reported tertiary resin alcohol, diphenyl-*t*-dehydroabietinol (I),[1] has been subjected to chromic acid oxidation in glacial acetic acid from which the cyclic ketone, 1-keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (II), is obtained in yields as high as 67%, together with benzophenone. It is to be noted that this oxidation differs from the Barbier–Wieland type of oxidative degradation in that there cannot be a preceding dehydration of the carbinol to an olefin, since no hydrogen atoms are attached to the carbon atoms at which oxidation occurs.



Fifteen years ago Vocke[2] submitted the diphenyl carbinol of tetrahydroabietic acid to the

---

[1] Paper I, THIS JOURNAL, **69**, 302 (1947).

[2] Vocke, *Ann.*, **497**, 247 (1932).