from the solution of decomposition products. The solution was first washed with sodium bicarbonate and treated with mercury to remove acid and iodine.

The infrared spectrum of the ester is identical with that of the synthetic β-iodoethyl β-iodopropionate. It was further identified by saponification to β-iodoethanol and β-iodopropionic acid, identified by infrared spectrum and mixed melting point. Before molecular distillation, the infrared spectrum of the nonvolatile products resembled those of model alkyl acyl carbonates.[12] It had bands at 3600 cm.$^{-1}$ (w), 2900 cm.$^{-1}$ (w), 1820 cm.$^{-1}$ (w), 1740 cm.$^{-1}$ (s), 1410 cm.$^{-1}$ (m), 1370 cm.$^{-1}$ (w), 1350 cm.$^{-1}$ (w), 1330 cm.$^{-1}$ (w), 1270 cm.$^{-1}$ (m) (shoulder), 1230 cm.$^{-1}$ (s), 1090 cm.$^{-1}$ (s), 1050 cm.$^{-1}$ (s) (shoulder), 930 cm.$^{-1}$ (w), and 800 cm.$^{-1}$ (w). In one experiment, this ester precursor was observed to evolve gas spontaneously after the solvent had been removed *in vacuo* and while the residue was being allowed to warm up to room temperature. Thereafter it had a spectrum identical to that of the synthetic β-iodoethyl β-iodopropionate. An attempt to repeat this delayed carbon dioxide evolution quantitatively, with absorption of the carbon dioxide in barium hydroxide, gave a yield of barium carbonate of only 7%.

Kinetics.—Degassed runs were done in ampoules, each containing slightly more than enough for one analysis. The ampoules and their contents were degassed by the usual freezing and thawing cycles on a vacuum line. After removal from the thermostat, the ampoules were quenched by rapid cooling to room temperature. *Non-degassed* runs were carried out using a single flask fitted with a condenser above the bath level. Aliquots were removed by pipetting and quenched by rapid cooling.

Total peroxide plus free iodine was determined by adding a 1.00-ml. aliquot to 10 ml. of aqueous acetone potassium iodide solution and titrating the resulting iodine solution with sodium thiosulfate. Free iodine was determined by adding a 1.00-ml. aliquot to 10 ml. of acetone and then rapidly titrating the resulting solution with sodium thiosulfate. Control experiments using solutions made by mixing iodine and peroxide solutions of known concentration gave peroxide concentrations with a mean 1.5% error, and iodine concentrations with a mean 2.9% error.

Substituent Effects on Free Radical Formation[1]

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The ease of attack of a *tert*-butoxy radical on a series of monosubstituted cyclohexanes has been measured, both neat and in benzene. The attacking radicals were formed by the thermal decomposition of *tert*-butyl peroxide, and the measurements made by gas chromatographic analyses of the relative amounts of *tert*-butyl alcohol and acetone formed. Consideration of the results with regard to relative reactivities, solvent effects, Hammett equation relationships, and radical complexing suggests that the inductive effect of the substituent determines the ease of C—H bond breaking.

Previous studies[3] on the rates of hydrogen atom abstraction from various compounds by atoms and radicals yielded data which indicated the reactivities of the hydrogens were affected by resonance, steric, polar, and solvent effects. This investigation was concerned with the effect of substituents upon the reactivities of C—H bonds, in an aliphatic system, toward hydrogen atom abstraction by *tert*-butoxy radicals in solution. It appeared that a good measure of the inductive and resonance effects, with an approximately constant steric effect, could be obtained for a number of monosubstituted cyclohexanes. This could be obtained from a series indicating the ease of hydrogen atom abstraction from the variously substituted cyclohexanes relative to abstraction of a hydrogen atom from cyclohexane. Adopting Russell's[4] postulate that the relative importance of polar and resonance effects in determining the reactivity of C—H bonds may be separated by observations on the magnitude of the solvent effect, the same compounds were caused to react with the *tert*-butoxy radicals in benzene and carbon tetrachloride solvents.

Results

The reactivities of the carbon–hydrogen bonds toward *tert*-butoxy radicals have been determined for a series of substituted cyclohexanes. The *tert*-butoxy radicals were formed by the decomposition of *tert*-butyl peroxide in solutions of the various compounds studied. This decomposition was assumed to proceed in the following manner

$$(CH_3)_3CO{-}OC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3CO{-}H + R\cdot$$

$$(CH_3)_3CO\cdot \xrightarrow{k_3} CH_3COCH_3 + CH_3\cdot$$

The ratio of rates may be determined by measuring the amount of *tert*-butyl alcohol and acetone produced. In order to obtain the correct concentration of reactant in moles/liter, measurements were taken on the compounds studied to determine the volume change for each compound from room temperature to 135°, the reaction temperature. From these data and the densities at room temperature, the concentration of each of the compounds at 135° could be calculated. The amount of expansion was found to be approximately 12%

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[1] From the M.S. thesis of E. L. P., University of Connecticut, 1961.

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[3] (a) R. L. Huang and S. Singh, *J. Chem. Soc.*, 891 (1958); (b) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); (c) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958); (d) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957); (e) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959); (f) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).

[4] G. A. Russell, *ibid.*, **80**, 4997 (1958).

TABLE I

HYDROGEN ABSTRACTION REACTIONS OF SUBSTITUTED CYCLOHEXANES

Compound	A k_2/k_3 ratios (neat)	B k_2/k_3 ratios in benzene	C Relative reactivities (neat)	D Relative reactivities (benzene)	E Per cent change due[a] to benzene solvent	F k_2/k_3 ratios corrected for complexing
Cyclohexane	1.87	1.59	1.00	1.00	...	...
Methoxycyclohexane	3.11	2.03	1.66	1.28	22.9	2.39
Ethylcyclohexane	2.32	1.61	1.24	1.01	18.5	1.89
Methylcyclohexane	2.09	1.44	1.12	0.906	19.1	1.70
Chlorocarbonylcyclohexane	1.41	1.25	0.754	.786	4.25	1.47
Acetylcyclohexane	1.39	1.13	.743	.710	4.44	1.33
Acetoxycyclohexane	1.30	1.01	.695	.635	8.63	1.19
Hydroxycyclohexane	1.15	0.840	.615	.528	14.12	0.990
Phenylcyclohexane	1.38	1.25	.739	.786	9.40	1.47
Chlorocyclohexane	1.09	.718	.583	.452	22.5	.845
Methoxycarbonylcyclohexane	0.996	.973	.533	.612	14.8	1.14
Cyanocyclohexane	.587	.573	.314	.360	14.65	0.675
Carboxycyclohexane	.507	.293	.271	.184	32.1	.345
Nitrocyclohexane	.329	.282	.176	.177	0.568	.332
Aminocyclohexane	.985	.770				
Methylaminocyclohexane	.860	5.75				
Dimethylaminocyclohexane	1.68	6.03				

[a] Calculated using columns C and D.

in all cases. The k_2/k_3 ratios have been calculated from the above equations and corrected for the effect of the chromatographic column on the ratio of alcohol to acetone obtained. These results are summarized in Table I, column A. The effect of solvents, benzene and carbon tetrachloride, was also determined for this same series of compounds. The same equations were used to calculate k_2/k_3 ratios and the ratios were corrected for the different amount of attack on benzene with respect to that on a hydrocarbon. However, the results from carbon tetrachloride were inconclusive and are not included. The results for the benzene solvent are shown in Table I, column B.

Discussion

The results presented in Table I suggest that the substituents govern the breaking of a C—H bond, by the *tert*-butoxy radicals, through their inductive effects. This will be shown to be reasonable by a consideration of: (1) the relative reactivities, (2) the solvent effects, (3) the rho value of the Hammett–Taft relationship obtained from the data, and (4) the effect of the complexing of the *tert*-butoxy radical. To be able to discuss these topics more readily, the results obtained, both neat and in benzene, are depicted relative to cyclohexane in Table I, columns C and D, respectively. From these data, the effect of benzene on the reactivity of the *tert*-butoxy radical toward a C—H bond is shown.

In order to understand the results, the transition state for the attack of a *tert*-butoxy radical on a C—H bond should be considered as[5]

$$\mathrm{X\cdot} + \mathrm{RH} \longrightarrow \underset{\mathrm{I}}{(\mathrm{R{:}H\cdot X}} \longleftrightarrow \underset{\mathrm{II}}{\mathrm{R\cdot\ {}^{+}H\ X{:}^{-}}} \longleftrightarrow$$

$$\underset{\mathrm{III}}{\mathrm{R\cdot H{:}X)}} \longrightarrow \mathrm{R\cdot} + \mathrm{HX}$$

Structure I should be important when there is little bond breaking in the transition state (where a polar reaction may be expected). Structure II should be important when X· has a high electron affinity and when the C—H bond has the highest availability of electrons. Structure III should be important if there is considerable bond breaking in the transition state (due to attack of a less electrophilic radical and formation of a resonance stabilized free radical). It has been suggested that resonance effects are not very important in the attack of a chlorine atom on most C—H bonds (since Cl· is so reactive)[6] and that the *tert*-butoxy radical has a reactivity comparable to the chlorine atom.[3e,7] Therefore, in the attack of a *tert*-butoxy radical the contribution of structure III should be relatively small. In terms of Hammond's[8] postulate, when X· is reactive the transition state will resemble reactants, whereas when the reactivity of X· is low the stability of the product is important and the transition state resembles the products.

The fact that electron-releasing substituents, such as methyl and ethyl, yield relative reactivities greater than that of cyclohexane, whereas electron-withdrawing substituents, such as cyano and nitro, have values less than cyclohexane, indicates that the relative reactivities are determined by the inductive effects of the substituent groups. It would follow that structure II contributes heavily to the transition state, since methyl and ethyl would favor a positive charge on R and an excess electron density at the C—H bond being attacked. This makes it easy for a hydrogen atom to be abstracted and thus increases the k_2/k_3 value. The cyano and nitro group would remove electron density from the C—H bond being attacked and

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(5) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(6) G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

(7) K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

(8) G. S. Hammond, *ibid.*, **77**, 334 (1955).

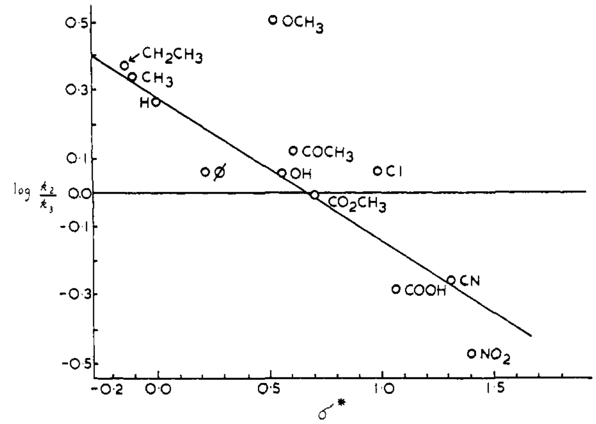

Fig. 1.—Reaction of *tert*-butoxy radicals with substituted cyclohexanes.

thus favor the decomposition reaction of the *tert*-butoxy radical, thereby lowering the value of the relative reactivity. As would be expected, the most powerful electron-withdrawing groups have the lowest values.

Russell[4] has postulated that the relative importance of polar and resonance effects in determining the reactivity of C—H bonds toward the chlorine atom may be separated by observations on the magnitude of the solvent effect. He suggests that if the reactivity is determined chiefly by polar effects the relative reactivities are not particularly sensitive to solvent effects (1–5-fold change), whereas, if the relative reactivities are determined by resonance stabilization solvent effects are large (20–225-fold change). The assumption was made that the effect would also hold for the *tert*-butoxy radical.[3e,7] Accordingly, the benzene and carbon tetrachloride solvents were used in this work to determine whether the relative reactivities of the C—H bonds were determined by polar effects of the substituents or by resonance stabilization of the resulting free radical. The results show that the values are determined by the polar effect of the substituent group, for the solvent effect of benzene is relatively small as can be seen from the percentage of change for each relative reactivity value, as given in Table I, column E.

The data listed in Table I, column A, were of such a nature that a Hammett equation evaluation could be made. The choice of the substituent constant to be used was open to question, since Walling[9] found that σ and not σ^* correlated better the data obtained from the attack of the *tert*-butoxy radical on substituted toluenes. Plots were drawn using σ, σ^+, σ_I, and σ^* *vs.* log k_2/k_3 values; all of these plots gave the same general conclusions. Since the polar effects seemed to be of greater influence and an aliphatic system was involved in the present study, the σ^* values[10] were chosen for the Hammett plot to evaluate the data. The plot obtained is shown in Fig. 1.

The ρ^* value of -0.43 obtained from Fig. 1 can be compared to the ρ values of -0.83 and -0.5 as found by Walling[9] and Williams,[11] respectively. The important conclusion, which must be made from the sign of rho, is that the carbon from which the hydrogen is being abstracted requires a high electron density in the transition state. Any decrease in the electron density by the inductive effect of a substituent would be expected to hinder the abstraction reaction.

In previous studies,[3e,12] the free radical reactivity values obtained when benzene was used as a solvent were consistently lower than those obtained neat. This was explained by assuming that the *tert*-butoxy radical forms a π-complex with the aromatic solvent which makes the radical less reactive and favors the decomposition reaction, k_3. It has been suggested that the transition state for the hydrogen abstraction reaction of the complexed *tert*-butoxy radical is closer to products and this would involve more resonance stabilization of the free radical being formed (more of intermediates II and III). Thus, enhanced reactivities should be found for those substituted cyclohexanes in which the substituent can readily stabilize the new free radical by conjugation.

To ascertain whether the present results compare with the above ideas, a comparison of the relative reactivities of the compounds neat and in benzene solvent must be accomplished as follows. The k_2/k_3 value for cyclohexane is smaller in benzene than in cyclohexane alone and since it can be assumed that there are no polar or resonance effects to consider in cyclohexane, the difference between these values is due to the complexing of the *tert*-butoxy radicals with the solvent, which favors decomposition to a methyl radical and acetone. Multiplying all the other k_2/k_3 values obtained in benzene by 1.87/1.59 (the ratio of k_2/k_3 value for cyclohexane alone to that in benzene) nullifies the amount of complexing with the solvent which results in excess acetone. The new reactivities are shown in Table I, column F.

The relative reactivities obtained differ only to a small extent from those obtained without any solvent. If the assumption on solvent effects is correct, one can conclude that there is little contribution from structures II or III in the transition state. The values, in benzene, for the groups that could show a resonance contribution are effectively the same as those with no solvent. This would again suggest that in these compounds the activity of the carbon–hydrogen bond is being determined mainly by polar effects.

The four methods of evaluation of the data were

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(9) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6113 (1960).

(10) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

(11) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).

(12) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

consistent in that they all indicated that the inductive effect of the substituent is of greater importance in hydrogen atom abstractions with a *tert*-butoxy radical. Since the inductive effect of the electron-withdrawing group on the C—H bonds is least on the hydrogens in the 4-position and greatest on the hydrogen in the 1-position, it could be considered that most of the attack of the butoxy radical would be away from the 1-position of the cyclohexane. This can be more readily visualized if a transition state with some of its structures is examined. Structures I, II, and III, above, differ in the arrangement of the electrons, and II involves an incipient positive charge on the carbon. When Z is NO_2, structure II would be of very high energy because the electron-withdrawing power of the nitro group increases the positive character of the carbon, and the radical would not form readily, as was found. It would be expected that attack would be on the 4-position, since it is deactivated the least. When Z is CH_3, the 1-carbon–hydrogen bond should be easily broken and the 1-methylcyclohexyl radical should be formed.

Alternative explanations can be considered, but they do not agree as well with the evidence. One possibility which can be suggested is that only the 1-hydrogen is abstracted as a result of the resonance stabilization of the radical formed, and the difference in reactivity is due to the inductive effect of the substituents. For example, when Z is NO_2 the resonance effect activates the 1-hydrogen the most while the inductive effect deactivates the 1-hydrogen the most, giving a low reactivity value. However, if both the solvent effect and the complexing effect previously discussed are correct, they require that little resonance stabilization of the substituted cyclohexyl radical in the transition state be involved.

No valid results were obtainable from the reaction of the compounds in carbon tetrachloride as the solvent, as only charred and tarry material was obtained. It is reasonable that a chain reaction which results in the formation of 1-chloro-1-substituted cyclohexene be involved.[13] This disubstituted compound would not be too stable.

Also, no meaningful data could be obtained from the reactions run with the amines. Abnormally large values were obtained in some cases. Therefore, samples of each of the amines were mixed with a known ratio of alcohol to acetone and gas chromatograms were taken to obtain the ratio before and after heating the mixtures. In the case of aminocyclohexane the amount of alcohol formed was nearly doubled after heating, and with methylamino- and dimethylaminocyclohexane, the amount of alcohol was reduced approximately in half after heating. After correcting the k_2/k_3 values obtained for these effects, the results were still random and appear to be in error to an unknown degree.

Experimental

The following compounds were used without further purification: acetylcyclohexane (Monsanto Chemical Co.), and thionyl chloride (Eastman Kodak Co., White Label).

The following compounds were distilled prior to use: phenylcyclohexane [Eastman Kodak Co., White Label, b.p. 45° (0.25 mm.), n^{25}D 1.5240], hydroxycyclohexane [The Matheson Co., Inc., b.p. 57.5–57.8° (8 mm.), n^{37}D 1.4610], chlorocyclohexane [Halogen Chemical Inc., b.p. 44° (25 mm.), n^{20}D 1.4630], *tert*-butyl peroxide [Lucidol Corp., b.p. 43.2° (67.5 mm.), n^{20}D 1.3893], ethylcyclohexane [Matheson, Coleman and Bell, b.p. 36.5–38.8° (26 mm.), n^{20}D 1.4330], benzene (Fisher Scientific Co., b.p. 80°, n^{20}D 1.5010), carbon tetrachloride (Baker and Adamson, reagent grade, b.p. 76.4°, n^{15}D 1.4630), methylcyclohexane (Eastman Kodak Co., White Label, b.p. 100°, n^{20}D 1.4232), cyclohexanecarboxylic acid [Eastman Kodak Co., White Label, b.p. 60–61° (0.09 mm.), $n^{33.8}$D 1.4560], nitrocyclohexane [Aldrich Chemical Co., Inc., b.p. 24–26° (0.09 mm.), n^{19}D 1.4612], aminocyclohexane [Eastman Kodak Co., White Label, b.p. 41–41.5° (23 mm.), n^{24}D 1.4570], and methylaminocyclohexane [Matheson, Coleman and Bell, b.p. 41° (12 mm.), n^{25}D 1.4540].

Cyclohexane (Fisher Scientific Co., reagent grade, b.p. 80°, n^{20}D 1.4260) was distilled through a Podbielniak concentric tube column (Model No. 2208).

Preparation of Compounds. Methoxycarbonylcyclohexane.—By the Fischer-Speier esterification process: A reaction mixture of cyclohexanecarboxylic acid (85.0 g., 0.67 mole), methanol (150.0 g., 5.0 moles), and concentrated sulfuric acid (1.65 ml., 0.03 mole) was heated at reflux for 24 hr. with stirring. The excess alcohol was removed by evaporation and the reaction mixture was placed in water and extracted with ether. After washing with water and removing the ether by evaporation, the solution was dried and distilled to yield 59.7 g. (63%) of methoxycarbonylcyclohexane, b.p. 44–45° (8 mm.), n^{25}D 1.4413, (lit.,[12] b.p. 183°, n^{25}D 1.4412).

Methoxycyclohexane and acetoxycyclohexane were prepared by the methods described by Vogel.[14]

Chlorocarbonylcyclohexane was prepared as described by Baumgarten.[15]

Cyanocyclohexane.—Excess thionyl chloride (47.59 g., 0.4 mole) was added to cyclohexanecarboxamide (29.68 g., 0.233 mole) and the mixture heated at reflux for 6 hr. The excess thionyl chloride was removed under reduced pressure. The resulting mixture was distilled to give 18.26 g. (71.8%) of cyanocyclohexane, b.p. 27-28.5° (0.1 mm.), n^{25}D 1.4492, [lit.,[15] b.p. 69–70° (12 mm.), n^{25}D 1.4493].

Dimethylaminocyclohexane.—Aminocyclohexane (49.6 g., 0.5 mole) was added to formic acid (59.75 g., 1.3 moles) at 5° and to this mixture 40% formalin (89.50 g.) was added still keeping the temperature between 5–10°. The mixture was heated at 90–95°, cooled to 50° and concentrated hydrochloric acid (62.0 g., 1.7 moles) was added. The excess formalin and formic acid was removed, 25% sodium hydroxide added, and the mixture distilled to give 33 g. (52%) of dimethylaminocyclohexane, b.p. 158.5–160°, n^{20}D 1.4519, lit.,[16] b.p. 75° (47 mm.), n^{25}D 1.4517.

Determination of the Relative Reactivities.—The following procedure was used for each compound studied: A standard amount of *tert*-butyl peroxide was weighed out individually into glass ampoules. In each of these ampoules enough of a single compound was weighed out to give, as close as possible, a 50:1 molar ratio of the individual

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[13] F. O. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1205 (1950).

[14] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

[15] H. E. Baumgarten, F. H. Bowers, and T. T. Okamoto, *J. Am. Chem. Soc.*, **79**, 3145 (1957).

[16] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

TABLE II

EXPERIMENTAL DETAILS AND RESULTS

Compound	Alcohol/Acetone ratio	Reactions done neat[a] k_2/k_3 uncorrected[c]	Column[d] effect	Per cent expansion 25 to 135°	Alcohol/Acetone ratio	Reactions done in benzene[b] k_2/k_3 uncorrected[c]	Column effect
Cyclohexane	18.2	2.27	1.83[e]	10.8	6.38	2.07	0.720[f]
Methoxycyclohexane	15.7	2.29	0.400[f]	...	5.68	1.97	.538[f]
Ethylcyclohexane	17.6	2.87	1.93[e]	...	4.73	1.77	.611[f]
Methylcyclohexane	16.9	2.47	0.643[f]	12.8	5.40	1.87	.823[f]
Chlorocarbonylcyclohexane	5.49	0.856	.988[e]	11.5	2.27	0.83	1.00[e]
Acetylcyclohexane	8.51	1.50	1.67[e]	...	3.09	1.15	0.567[f]
Acetoxycyclohexane	9.79	1.65	1.98[e]	...	2.83	1.04	.578[f]
Hydroxycyclohexane	1.82	1.21	1.64[e]	...	2.83	0.90	.605[f]
Phenylcyclohexane	7.16	1.41	1.59[e]	...	3.19	1.25	.55[d]
Chlorocyclohexane	14.8	1.28	0.636[f]	...	4.07	1.13	.898[f]
Methoxycarbonylcyclohexane	7.67	1.26	1.97[e]	13.5	2 91	1.06	1.70[e]
Cyanocyclohexane	4.41	0.588	1.66[e]	...	1.76	0.594	.578[f]
Carboxycyclohexane	3.59	.512	0.55[f]	...	1.27	.42	0.879[f]
Nitrocyclohexane	2.96	.477	2.19[e]	...	1.12	.376	2.34[f]
Aminocyclohexane	19.0	2.36	3.74[e]	12.9	9.52	3.08	6.25[e]
Methylaminocyclohexane	11.8	1.76	3.19[e]	...	14.7	5.17	1.40[e]
Dimethylaminocyclohexane	21.0	3.54	3.28[e]	...	19.80	7.25	1.82[e]

[a] The ratio of compound to peroxide was approximately 50:1, for example with cyclohexane the amounts were 0.018 mole:0.000355 mole. [b] All reactions were done in 5 ml. of benzene and the ratio of reactants was 25:1; with cyclohexane the amounts were 0.0275 mole:0.011 mole. [c] The k_2/k_3 values corrected for the changes caused by the chromatography column are given in Table I. [d] These were determined by measuring the change which resulted when a known ratio of alcohol:acetone was chromatographed in a blank. [e] Standard solution with alcohol:acetone = 1.56. [f] Standard solution with alcohol:acetone = 0.545.

compound to the *tert*-butyl peroxide. All the samples were cooled in a chloroform–carbon tetrachloride–Dry Ice-cooling bath, flushed with argon, and sealed. The samples were placed in an oil bath at 135 ± 2° for 48 hr., which corresponds to approximately ten half-lives and the decomposition of 99.9% of the peroxide. After cooling in the previously mentioned cooling bath, the seals were broken and the contents of each ampoule were analyzed by gas chromatography. The ratios of *tert*-butyl alcohol to acetone were obtained from the chromatograms (Aerograph Model 90-C., Leeds and Northrup 1 mv. recorder, equipped with a Disc Integrator, 10-ft. Ucon polar column, 85–156°, 5–10 p.s.i. He, 200 ma.). The concentrations of the different compounds were calculated from the known weights and the volume at 135°. The results are summarized in Table II.

The following procedure was used for each compound studied to determine the effect of benzene and carbon tetrachloride solvents on the ratios obtained: A standard solution of *tert*-butyl peroxide in benzene or carbon tetrachloride was prepared; 5.0 ml. of this solution was pipetted into each of the glass ampoules which contained a weighed sample of compound, so that the molar ratio of compound to *tert*-butyl peroxide would be 25:1. The ampoules were then treated in the manner described above. The contents of each ampoule were analyzed by gas chromatography. In the case of carbon tetrachloride as the solvent, no reliable results were obtained since many of the compounds charred or gave various undesirable decomposition products. The ratios of *tert*-butyl alcohol to acetone and the concentrations of the various compounds were calculated as described above. The results are summarized in Table II.

In order to determine whether the *tert*-butyl alcohol to acetone ratios were affected by the various compounds and the column, solutions of known molar concentrations of *tert*-butyl alcohol and acetone were made up and analyzed by gas chromatography to obtain the standard ratio. A few drops of this solution were added to each compound and these solutions were analyzed by gas chromatography under the same conditions as the reaction mixtures themselves. The results are shown in Table II.

Determination of Volume Change of Samples with Temperature.—In order to determine the volume expansion of the compounds used in this study the following procedure was used: A measured amount of the compound was placed in a 1-ml. Pyrex pipet graduated in 0.01 ml., one end of which was sealed and a reading was taken. The mixture was cooled in a chloroform–carbon tetrachloride–Dry Ice bath and the other end sealed. These tubes were placed in an oil bath at 135 ± 2° for 45 min. and a reading was then taken. The expansions were found to be approximately 12% for the compounds and are summarized in Table II.

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