pentadienylidene-1,2-dihydropyridine compared to that for 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole is interpreted to reflect a more significant pyridinium resonance contribution to the transition state than to the ground state. It might be anticipated that the transition state for this process in 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine should be approximately the resonance energy of pyridine lower than that for 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole. The observed difference in activation energies for these two systems (8.2 kcal) indicates that in the transition state the expected additional pyridinium resonance stabilization is not fully realized because energetically it is partially lost as additional electrostatic work necessary to separate a greater amount of charge over a greater distance.

## Experimental Section

All nmr spectra were determined on a Varian Model HA-100 spectrometer equipped with a variable-temperature probe. The computations were performed on an IBM Model 360/50 computer. The carbon and hydrogen analysis was performed by Galbraith Laboratories Inc., Knoxville, Tenn.

**1-Methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (3).** Cyclopentadiene (13.3 g, 0.2 mole) was added dropwise with stirring to a suspension of sodium hydride (4.8 g, 0.2 mole) in 50 ml of tetrahydrofuran, under nitrogen. A mixture of N-methyl-2-pyrrolidone (19.8 g, 0.2 mole) and dimethyl sulfate (25.2 g, 0.2 mole) was heated for 20 min on a steam bath. The resulting complex was added dropwise to the sodium cyclopentadienide solution which was cooled to −5° in an ice–salt bath. After the resulting mixture had stirred *ca.* 2 hr, the suspension was filtered, and the resulting brown solution was concentrated on a rotary evaporator. This yielded a brown oil which solidified on cooling. This material was recrystallized two times from cyclohexane to give pale yellow needles (14.0 g, 50%) of 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (mp 100–101°). Carbon and hydrogen analyses were consistent with the molecular formula.

The remaining two compounds were prepared by methods reported in the literature and exhibited physical properties consistent with those reported.

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# Crowded Benzenes. VI.[1] The Strain Energy in *o*-Di-*t*-Butylbenzenes[2]

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**Abstract:** The standard strain energy, $\Delta H_{\text{strain}}$, of *o*-di-*t*-butylbenzene (ODTB) is defined as the difference in standard heat of formation of this compound and its *para* or *meta* isomer (PDTB or MDTB). On the basis of the following evidence, $\Delta H_{\text{strain}}$ for this system is found to be 22.3 ± 0.5 kcal/mole, which is close to Brown's estimate. ODTB is converted rapidly and exothermically by aluminum bromide in carbon disulfide to a variety of products whose number and nature depend on [$AlBr_3$]. PDTB or MDTB yields the same array of products as ODTB (or products of equivalent heat of formation) under the same conditions. When the calorimetrically determined heats of reaction are corrected for heats of solution in $CS_2$ alone, their difference may be related directly to $\Delta H_{\text{strain}}$ in the gas phase because the heats of vaporization and complexing with aluminum bromide are nearly equal for liquid, unstrained, isomeric dialkylbenzenes. Even though the heats of reaction and product yields for both isomers are sensitive to [$AlBr_3$], over 37 products being formed at the highest concentration, the *difference* between their heats of reaction is invariant to conditions. This indicates that there is a single large energy difference between them and this we equate to $\Delta H_{\text{strain}}$. $\Delta H_{\text{strain}}$ for 1,2,4-tri-*t*-butylbenzene (TTB) (relative to 1,3,5-TTB) is estimated in the same way to be 22.3 ± 1 kcal/mole. This value is reconciled with a previous estimate by a correction for heat of sublimation. Furthermore, mass spectral comparisons of (P − 15) appearance and ionization potentials for ODTB *vs.* PDTB or MDTB and of 1,2,4-TTB *vs.* 1,3,5-TTB indicate an energy difference of about 20 kcal/mole. $\Delta H_{\text{strain}}$ is more than half the usually accepted resonance energy of benzene. However, there is no evidence from nmr, infrared, or electronic spectra or from the reactions of compounds containing the *o*-di-*t*-butylbenzene system that a "nonaromatic benzene" has been produced by warping the ring. The only indication for loss of aromatic character is a 30% decrease (relative to benzene) in Dauben's diamagnetic susceptibility exaltation.

Over a decade ago, Brown and his students[4–7] deduced by their method of homomorphic analogy that aromatic compounds carrying two *t*-butyl groups in an *ortho* arrangement should be destabilized by strain energy amounting to at least 25 kcal/mole. The pos-

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[1] For previous paper in this series, see E. M. Arnett, J. M. Bollinger, and J. C. Sanda, *J. Am. Chem. Soc.*, **87**, 2050 (1965). Requests for reprints should be sent to E. M. A.

[2] Presented in preliminary form at the Benzene Centennial Symposium on Aromatic Character and Resonance, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965. Most of the material in this paper is taken from the thesis of J. C. Sanda, University of Pittsburgh, 1966.

[3] This research was supported mostly by U. S. Public Health Service Fellowship 5-F1-GM-19, 792-04 from the National Institute of General Medical Sciences and in its early stages by Grant No. 354 of the Petroleum Research Fund of the American Chemical Society, National Institutes of Health Grant CA-05512, and National Science Foundation Grant 14583. Grateful acknowledgment is made to the donors of these grants.

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sibility that this estimate was too high soon arose when the difference in heats of hydrogenation between *cis*- and *trans*-di-*t*-butylethylene was found to be about 10 kcal/mole.[8–10] It seemed likely that synthesis of *o*-di-*t*-butyl aromatics would require special methods to avoid product-forming transition states with direct confrontation of an attacking *t*-butyl cation or radical and an adjacent bulky group. This agrees with the fact that all reports in the older literature of the Friedel–Crafts syntheses of compounds carrying very bulky groups *ortho* to each other have been proven incorrect.[11–17] The papers of Brown and Newman drew the attention of several research groups to the interesting chemical, physical, and physiological[18] properties that might result from a highly strained and possibly warped[19–24] aromatic system. In the ensuing years, a number of aromatic hydrocarbons carrying *o*-di-*t*-butyl functions have been synthesized, mostly by means of special cyclization reactions.[25–32]

Hübel and his co-workers reported estimates of the strain energy of 1,2,4-tri-*t*-butylbenzene[25] (relative to its 1,3,5 isomer) to be 16.8 ± 1.7 kcal/mole and of 1,2,4,5-tetra-*t*-butylbenzene[27] (relative to a hypothetical uncrowded model) to be 31.0 ± 3.7 kcal/mole. These values were based on heat of combustion measurements[33] and suffer from two shortcomings as the authors carefully pointed out. Firstly, the strain energies are relatively small differences between two very large numbers, *ca.* 3000 kcal/mole. Secondly, there are unknown contributions from different heats of sublimation since the standard states were the pure, crystalline compounds. Subsequently, Karnes, Kybett, Wilson, Margrave, and Newman[34] estimated the vapor-phase strain energy of 4,5-dimethylphenanthrene (relative to the 2,7 isomer) to be 12.6 ± 1.5 kcal/mole, again by heats of combustion but with corrections for heat of sublimation. They considered this to be a lower limit for the 4,5-dimethyl repulsion. Newman[35] had previously drawn attention to the large (6–8 kcal/mole) effects that can arise from heats of fusion of crystalline strained compounds.

These various estimates all indicate that at least 10 kcal/mole of strain energy is distributed through the *o*-di-*t*-butylbenzene system and the uncertainty is such that it may be a good deal more. On the other hand, the spectra[19–31] and chemical reactivity[36] give little evidence of this being an abnormal aromatic system (see Discussion). In particular, there is no compelling evidence that the ring is warped severely so as to cause double bond fixation[19–21] in what might be called a "nonaromatic benzenoid hydrocarbon." The apparent conflict of these results suggest that either all estimates of the strain energy in *o*-di-*t*-butylbenzenes are too high or that the strain is absorbed mainly in distortions of the *t*-butyl groups without loss of ring aromaticity.

The point at issue is important since two of the most potent driving forces in organic chemistry, steric repulsion and resonance stabilization, are forced here into direct confrontation. With estimates of the former ranging from 30[8,9] to 60%[4–7] of the latter,[37] it seemed worthwhile to estimate directly the strain energy in *o*-di-*t*-butylbenzene relative to its *para* isomer. Our point of departure was Olah's observation[38] that both *ortho* and *para* isomers react very rapidly with aluminum chloride in carbon disulfide to yield similar products. The difference in the heats of the two reactions may then be related directly (see Results) to the strain energy.

## Experimental Section

**1. Materials.** The following abbreviations will be used henceforth for the compounds discussed in this paper: ODTB, *o*-di-*t*-butylbenzene; MDTB, *m*-di-*t*-butylbenzene; PDTB, *p*-di-*t*-butylbenzene; TB, *t*-butylbenzene; DUR, durene; 135-TTB, 1,3,5-tri-*t*-butylbenzene; 124-TTB, 1,2,4-tri-*t*-butylbenzene.

Aluminum bromide (Fisher, ACS Reagent Grade) was completely soluble in carbon disulfide and was used without purification. Carbon disulfide (Baker and Adamson, ACS Reagent Grade) was dried over activated Linde Type 5A Molecular Sieves. It, and all of the following hydrocarbons, were tested carefully for purity by glpc on both the instruments to be described and had the physical properties shown, after conventional purification. DUR (Shell) had mp 78–79°[39a] and TB (Eastman), $n^{20}\mathrm{D}$ 1.4922.[39b] PDTB, mp 77.0–77.5°,[39c] and 135-TTB, mp 71.6–72.2°,[16] were generously supplied by Drs. A. A. McCaulay and R. W. Todd, American Oil Co., Whiting, Ind. 124-TTB, mp 47.8–48.2°, was prepared by the method of Hübel.[25] MDTB was made by isomerization of the *para* isomer[38] and isolated by preparative glpc, $n^{20}\mathrm{D}$ 1.4878.[40]

ODTB was prepared by the procedure of Burgstahler and Abdel-Rahman.[31] In our hands, serious reductions in yield resulted from tenfold scale-up. Especially serious losses occurred in the Friedel–Crafts cyclization of 2,2,5,5-tetramethyltetrahydrofuranone with benzene (13.5 *vs.* 30%[31]) and in the hydride reduction of $\alpha,\alpha'$-*o*-phenylenediisobutyraldehyde (42 *vs.* 92%[31]), due to formation of the cyclic lactol. Our yields agreed within 10% with those

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reported for the other steps and also for control runs without scale-up.[41] The final product was homogeneous on both gas chromatographs and showed correct physical properties, mp 26.5–27.5°, $n^{30}D$ 1.5150.

**Reactions of ODTB and PDTB with Hydroxylating Reagent.** A number of polyalkylbenzenes are converted to phenols by peroxytrifluoroacetic acid and boron trifluoride,[42] which presumably generate incipient hydroxy cation. We applied the reaction to ODTB and PDTB by preparing a 1.15 *M* stock solution of peroxytrifluoroacetic acid at 0° from 24.8 ml of methylene chloride, 0.992 ml ($3.67 \times 10^{-2}$ mole) of 90% hydrogen peroxide, and 8.70 g ($4.14 \times 10^{-2}$ mole) of trifluoroacetic anhydride (K & K Laboratories, Inc.). Stirring and warming to room temperature produced a homogeneous solution of which aliquots were added as follows, to ODTB, PDTB, and a hexamethylbenzene control[42] within 4 hr.

ODTB (3.15 equiv) was caused to react with 1.0 equiv of peroxytrifluoroacetic acid at 0° for 20 min while boron trifluoride was bubbled through the solution. Quenching of the black solution with water, extraction with methylene chloride, and evaporation gave a dark brown, oily residue from which upon subsequent recrystallization and silicic acid chromatography[41] could be obtained absolute yields of 53% MDTB, 10% PDTB, and traces of 135-TTB, TB, and 3,5-di-*t*-butylphenol, the rest of the product being intractable tar.

Upon identical treatment, PDTB could be recovered in 74% yield along with traces of *p*-*t*-butylphenol and 2,5-di-*t*-butylphenol.

The hexamethylbenzene control run gave yields identical with Hart's.[42] Treatment of ODTB with $BF_3$ alone under the above conditions gave no detectable product except starting material. ODTB and PDTB were also resistant to attack by monoperphthalic acid for 10 days at 4°.

**2. Calorimetry.** Calorimetric measurements were obtained in a solution calorimeter described in detail elsewhere.[43] For introduction of solids, a 2-ml B–D Multifit glass syringe with the end of the barrel sawed off was used in place of a polyethylene syringe since the latter is attacked by aluminum bromide.

In view of the low melting point of ODTB, heats of solution were made at 30 ± 0.5° where it is a liquid. The solvent to be used was warmed in a sealed dry flask to slightly above this temperature before introduction into the calorimeter. Tight seals at the calorimeter head were necessary to prevent cooling by evaporation of solvent and absorption of atmospheric moisture.

The effect of water on Friedel–Crafts reactions is complex, promoting catalyst activity at low water concentrations[38,44] and quenching it at higher ones. This factor was manifested by erratic $\Delta H_{\text{obsd}}$ measurements in the most dilute solutions ($\leq 4.2 \times 10^{-3}$ *M*) of aluminum bromide during warm, humid weather. It appeared to be an "all or none" phenomenon. Large and reproducible $\Delta H_{\text{obsd}}$ (see Table IV) were correlated directly with the occurrence of yellow to orange colors of $\sigma$ complexes.[44,45] In order to reduce this problem to the barest possible minimum, the following routine was followed for nearly all runs.

The dried (Molecular Sieves) carbon disulfide was tested for traces of moisture with fresh calcium hydride; the proper volume was measured into a dried 4-l. reservoir bottle which had been made to accommodate a sealed 100-ml "Geyromatic" automatic zero-reading buret (Scientific Glass Apparatus Company, Inc., Catalog No. JB-6990). Chunks of aluminum bromide were transferred under dried argon from the bottle in which it was purchased to a weighing bottle; traces of oxide were scraped off when detected. The weighing bottle, tweezers, beaker, and spatula used for the transfer were dried in a vacuum oven at 70° for 30 min with occasional purging by argon which had been dried by passage through a "Lectrodryer."[46] Whenever erratic results were encountered, the same drying technique was used for the reservoir bottle, magnetic stirrer, calorimeter assembly (dewar flask, stirrer, and Teflon head), thermometer, syringe, and all components that came in contact with the solution. It is not clear which precautions were really substantive, but this routine was effective in drastically reducing wasted runs. Aluminum bromide was weighed in a tightly stoppered bottle and dumped into the carbon disulfide in the reservoir. The residual contents of the weighing bottle were rinsed into the latter under argon with a known volume of solvent and stirred magnetically for 30 min. Stock solutions prepared in this way were colorless and contained only traces of aluminum oxide. They were protected by wrapping the reservoir with aluminum foil and keeping all access points sealed with clamps except during use when drying tubes and dried argon were used to exclude moisture. Unused solutions were discarded after a week. These precautions were often followed for the more concentrated aluminum bromide solutions even though they were not sensitive to traces of moisture. Since $\Delta H_{\text{obsd}}$ is not very dependent on [$AlBr_3$], small losses of catalyst through hydrolysis do not affect the results.

Measurements of $\Delta\bar{H}_s$ in pure carbon disulfide were not sensitive to moisture since no reaction was involved; therefore, no special precautions to maintain dryness were used for them.

In order to reduce the opportunity for hydrolysis during the calorimeter runs, heat calibration measurements[43] were limited to one before and one after each injection of the hydrocarbon substrate. Usually, only one injection of aromatic was made in each calorimeter full of fresh stock solution in view of the sensitivity of $\Delta H_{\text{obsd}}$ to [aromatic]. However, it was shown (see Results) that comparable values were obtained when three successive increments were injected into a single dewar full of the more concentrated solutions where [$AlBr_3$] = $27.2 \times 10^{-3}$ *M*.

In order to ensure complete delivery of liquid aromatics, the plunger of the Hamilton syringe was pumped five times while in place and the small heat of pumping was corrected for later by a control experiment.

**3. Gas Chromatography.** Product mixtures were separated at high resolution with a 200-ft Apiezon L capillary column leading to a hydrogen flame detector. The instrument was designed and built by Mr. L. V. Guild in this laboratory. Quantitative analysis of larger samples was accomplished with a Wilkens-Anderson aerograph A-700 using a 20 ft × $^3/_8$ in. column packed with 23% SE-30 on 30–60 mesh Firebrick. Peak areas were integrated with a digital or ball and disk integrator. Integrators and recorder attenuators were checked for linearity.

**4. Stoichiometry.** Our approach required that strained and unstrained isomers yield identical product mixtures after treatment with aluminum bromide. Therefore, accurate analysis of the products is as crucial as accurate measurement of the heat of reaction.

The following work-up procedure was followed ritualistically with only slight and deliberate deviations in special cases. These are described in detail in the thesis of J. C. S.[2]

Since the yields of products and heats of individual reactions were found to depend upon concentrations, reaction time, and exposure to moisture, no effort was spared to carry out stoichiometry runs under conditions identical with those used for calorimetry. In order to obtain meaningful analyses from the very low (*ca.* $10^{-3}$ *M*) initial concentrations of aromatics, the quantities (but not concentrations) of reagents were usually doubled.

About 300 ml of aluminum bromide stock solution, prepared and protected as described above, was drawn into a dried 500-ml separatory funnel (to be used as reaction vessel), stoppered, and warmed to 30.5° with hot air. The aromatic was then injected beneath the surface in the usual manner; the separatory funnel was stoppered and shaken vigorously for 30 sec at the end of which time the reaction was quenched by the addition of 35 ml of water. In all cases, the aromatic dissolved instantly, and the solution quickly developed a yellow or pinkish color which was quenched after two vigorous shakes with water. This was taken to be the end of the reaction time and corresponded to the period needed to reestablish a recorder base line on the calorimeter following the 2 or 3 sec of the first large exothermic displacement after injection of the strained isomer. The carbon disulfide solution was now washed thrice with water and twice with aqueous bicarbonate and rinsed with water. The aqueous layer was extracted with hexane which in turn was washed once. The nonaqueous layers were dried over sodium sulfate and calcium chloride, then most of the solvent was removed by distillation with magnetic stirring in a grease-free, ground-glass, 100-ml, round-bottomed flask with a 1-ft Vigreux column until the volume reduced to about 10 ml.

At this point the solution was evaporated at 105° from successive 3-ml increments in a 5-ml flask carrying a 2-in. column-distillation

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head and containing about 25 mg of DUR which had been weighed accurately into the flask for subsequent use as an internal glpc standard. Purified hexane was used for rinsing at each step to reduce transfer losses and hence was the chief component of the concentrated solution. The final solution was yellowish and often contained traces of a precipitate. This was shown by a control work-up experiment to be finely divided inorganic material.

## Results

1. **Rationale.** Determination of the strain energy by difference in heat of reaction between strained and unstrained isomers depends upon two types of information. First, reliable calorimetric measurements are needed for the reactions of the two isomers in solution. Second, we must show that both isomers yield identical product mixtures or products with equivalent heats of formation (see below). Furthermore, we must show that the product mixtures for both isomers vary in the same way with conditions or do not violate the requirements stated above. In order to minimize solute–solute interactions, the most dilute solutions of aromatic that were feasible for stoichiometry and calorimetry were used. A number of preliminary experiments indicated that aromatic concentrations in the neighborhood of $10^{-3}$ $M$ would give optimum results at 30° and 30-sec reaction time and that heats of reactions and product composition varied with the concentration of aluminum bromide. Accordingly, heats of reaction of both isomers were obtained at four catalyst concentrations from $1.06 \times 10^{-3}$ $M$ to $27.2 \times 10^{-3}$ $M$ holding all other conditions constant. Complete analyses of products were obtained at the two extremes of catalyst concentration. Although product compositions changed drastically and heats of isomerization of both isomers also varied as a function of catalyst composition, *the difference* in heat of reaction between the isomers remained constant at all four concentrations indicating that a single invariant heat contribution made the difference between them.

2. **Stoichiometry.** High sensitivity qualitative analysis with the capillary column unit was necessary to demonstrate that all of the strained isomer had reacted within the 30-sec reaction period and that both mixtures gave an identical array of products at the higher catalyst concentration. Under these conditions, there were so many trace quantities of minor products that a complete quantitative analysis was impossible.

3. **Qualitative Analysis.** A 200:1 stream-split ratio and nonlinear temperature programming were used. The column was held at 120° until TB was eluted, and then within 2 min was raised to 240° where it was held until the last product came off. Temperature programming was not required for the product from $1.06 \times 10^{-3}$ $M$ aluminum bromide, since only two to four products were detectable. In both cases, it was demonstrated that no ODTB remained after 30-sec reaction, within the limits of detection, *i.e.*, less than 0.8% could have remained. It was also shown in the case of 124-TTB that none remained within the limits of detection. Although absolute retention times were not very reproducible, those taken relative to the retention time of added DUR were good.

The product mixture from work-up of the reaction of ODTB and PDTB with $27.2 \times 10^{-3}$ $M$ aluminum bromide yielded many products on the capillary column. In order to discriminate between those from isomerization of the aromatic substrates and those introduced by work-up, a control test was run on a calorimeter full of standard $27 \times 10^{-3}$ $M$ aluminum bromide stock solution which was carried through all of the steps of work-up and analysis except that no aromatic was added to it. When accidental peaks, due to solvents and traces of impurities in them, were subtracted from the product chromatograms, it was found *that for both ODTB and PDTB an identical array of 37 products could be detected.* TB, MDTB, PDTB, and 135-TTB were shown to be present by relative retention times and by control experiments using enrichment with authentic compound.

A similar analysis (supplemented by collection and identification by infrared spectrum) of the products from isomerization with $1.06 \times 10^{-3}$ $M$ aluminum bromide solution yielded only four products from ODTB (TB, MDTB, PDTB, and 135-TTB) and only one product, namely TB, plus residual PDTB, from the *para* isomer. Thus, a 27-fold reduction in aluminum bromide concentration reduced the PDTB products from 37 to 1.

4. **Quantitative Analysis.** Quantitative glpc analysis was done as described under Experimental Section. Since only four products (TB, MDTB, PDTB, and 135-TTB) were formed at the lowest concentration, a reliable analytical procedure had to be developed for these mixtures in order to show that the heats of formation of the products in this case were identical from both isomers undergoing reaction. Approximate product compositions were obtained by preliminary analysis of the product mixture. Based on these, seven synthetic mixtures of the four product compounds were prepared covering the estimated ranges of the relative concentration of each of the four products. To the hexane solutions of these synthetic mixtures was then added a weighed amount of DUR and a number of replica analyses of each of the seven solutions were performed. From these results, a plot was prepared for the average weight (relative to that of DUR) for each component in the synthetic mixture *vs.* the average peak area (relative to DUR) for the same mixtures. Each of these four plots of relative weight *vs.* relative area was linear through the working range. These calibration plots of relative weight per relative area could then be used to estimate the relative weight of each component in any mixture analyzed under the same conditions.

In order to correct results obtained in this way to the weights of each product that were present in the freshly quenched reaction solution before work-up, a series of four synthetic solutions corresponding exactly in composition to the estimated product solution before work-up was prepared. This was then subjected to exactly the same work-up procedure as was applied to all quenched stoichiometry solutions and was analyzed as described above. From these results, a final small correction could be made to allow for differential work-up losses. The final results from duplicate runs using all precautions for the analytical methods described above for ODTB and PDTB are presented in Table I. Many replica measurements of both stoichiometric and calorimetric determinations over many months were made using different batches of material under widely different atmospheric conditions.

Although an identical mixture of over 37 products was found from treatment of ODTB and PDTB with $[AlBr_3] = 27 \times 10^{-3}$ $M$, Table I shows a clear difference

**Table I.** Corrected Weights and Yields of Products from Reactions of *o*- and *p*-Di-*t*-butylbenzene with 1.06 × $10^{-3}$ *M* Aluminum Bromide Solutions

| | | | Corrected wt, mg, and mole % yields of reaction products | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Aromatic reactant | Run | Initial wt, mg | TB Wt | TB % | MDTB Wt | MDTB % | PDTB Wt | PDTB % | 135-TTB Wt | 135-TTB % |
| ODTB | 3 | 88.6 | 13.4 | 21.5 | 22.2 | 25.1 | 43.6 | 49.2 | 4.0 | 3.4 |
| ODTB | 4 | 88.6 | 13.7 | 21.9 | 21.1 | 23.8 | 41.5 | 46.8 | 3.1 | 2.8 |
| PDTB | 2 | 88.1 | 12.5 | 20.1 | ... | 0.0 | 74.9 | 85.0 | ... | 0.0 |
| PDTB | 3 | 88.3 | 12.2 | 19.6 | ... | 0.0 | 70.9 | 80.3 | ... | 0.0 |

between the amount of MDTB and 135-TTB formed from them when [AlBr$_3$] = 1.06 × $10^{-3}$ *M*. The heat of formation of MDTB is almost surely equal to that of PDTB (see Discussion), so this poses no problem. The 3% difference in yield of 135-TTB probably has little effect on the heat of formation (Tables II and VII) or heat of complexing for the products. A detailed accounting for contributions to the total heat of formation of the products is given in Table II and shown to be identical within experimental error for the two isomers. The fate of 20 mole % of *t*-butyl cation from both compounds is unknown and is assumed to be independent of its origin.

**Table II.** Estimation of the Standard Heats of Formation ($\Delta H_f°$) of the Products from the Reactions of *o*- and *p*-Di-*t*-butylbenzene with 1.06 × $10^{-3}$ *M* Aluminum Bromide Solutions by Franklin's Method of Group Equivalents[a]

| | TB | MDTB | PDTB | 135-TTB | Estimated total $\Delta H_f°$ of products |
|---|---|---|---|---|---|
| $\Delta H_f°$, kcal/mole | −7.5 | −34.8 | −34.8 | −62.1 | |
| % yield of products from ODTB | 21.7 | 24.5 | 48.0 | 3.1 | |
| Contribution to $\Delta H_f°$ | −1.6 | −8.5 | −16.7 | −1.9 | −28.7 |
| % yield of products from PDTB | 19.9 | 0.0 | 80.3 | 0.0 | |
| Contribution to $\Delta H_f°$ | −1.5 | 0.0 | −27.9 | 0.0 | −29.4 |

[a] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).

Because of shortages of material, we were unable to make as exhaustive a stoichiometric study of the tri-*t*-butylbenzenes (124-, 135-TTB) as was possible for the di-*t*-butylbenzenes. However, product mixtures from several stoichiometric runs established qualitatively that at several widely spaced aluminum bromide concentrations, the two compounds were, in fact, giving similar yields of products. In this case, as for ODTB *vs.* PDTB, the strongest argument for the ultimate validity of calculation of strain energy is the fact that the difference in heats of isomerization at several different concentrations remained a single invariant value. The results of this study are presented in Table III. It will be noted that the only system in which both isomers are compared directly was that with 1.06 × $10^{-3}$ *M* aluminum bromide which, because of spoiling by adventitious moisture, could not be studied calorimetrically. At the higher [AlBr$_3$] where most calorimetric measurements were made, we did not have enough 124-TTB for stoichiometric measurements. The principal point of difference in the stoichiometry run at [AlBr$_3$] = 1.60 × $10^{-3}$ *M* was the loss of a tertiary butyl group from the 124-TTB, but not from its 1,3,5 isomer. At the higher catalyst concentration where calorimetric measurements were made the 1,3,5 isomer also lost a *t*-butyl group, suggesting that this difference between products was eliminated there.

**Table III.** Effect of Changing Concentration of Aromatic and Catalyst on Product Composition for Two Tri-*t*-butylbenzenes (TTB)

| TTB | [TTB] × $10^4$, moles/l. | [AlBr$_3$] × $10^3$, moles/l. | Products |
|---|---|---|---|
| 1,2,4 | 3.21 | 1.06 | TB (trace), MDTB (major), PDTB (minor) |
| 1,3,5 | 3.54 | 1.06 | TB (trace), MDTB (major), 1,3,5-TTB (major) |
| 1,3,5 | 3.58 | 4.22 | TB (trace), MDTB (major), PDTB (major) |

**5. Calorimetry.** Heats of isomerization and product yields were sensitive to time of reaction, temperature, and concentration. It was, therefore, important to control these variables carefully. All of the calorimetric runs to be described here were made at 30 ± 0.4° for 30 sec. All runs with the di-*t*-butylbenzenes employed samples weighing 44.3 ± 1.3 mg, injected into 175 ± 1 ml of aluminum bromide stock solution in carbon disulfide, as described above. The initial concentration of aromatics was therefore 1.33 × $10^{-3}$ *M* and [AlBr$_3$] was varied as described below. Recorder base lines before and after injection of the sample into the catalyst solution were never as straight as is customary in our apparatus.[43] Some curvature and drift was probably due to working above ambient temperature, using a highly volatile solvent, and perhaps having secondary reactions after the first major exothermic one.

Values for $\Delta H_{\mathrm{obsd}}$, the combined molar heat of solution and heat of reaction for the aromatics in the different aluminum bromide solutions, are presented in Table IV as are also values for $\Delta \bar{H}_s$, the partial molar heat of solution of the aromatic compound into carbon disulfide containing no aluminum bromide. This latter term is necessary to allow for the heat of vaporization or sublimation of the pure liquid or solid aromatic to the appropriate state of dilution in this solvent.

It will be noted that 12–18 independent measurements of $\Delta H_{\mathrm{obsd}}$ were made for the two key compounds. Ideally, these values should all have been determined in fresh solutions of aluminum bromide. However, many measurements were made using three consecutive injections of the aromatic compound into the same solutions of 27.21 × $10^{-3}$ *M* aluminum bromide in the hope that the later injections would be as reliable as the first ones. If this were true, the statistical sample could be

**Table IV.** Effect of Changing Concentration of Aromatic and Catalyst on Observed Heat of Reaction ($\Delta H_{\text{obsd}}$)

| Aromatic | $[\text{AlBr}_3] \times 10^3$, moles/l. | $\frac{[\text{AlBr}_3]}{[\text{aromatic}]}$ | No. of runs | $\Delta H_{\text{obsd}}$, kcal/mole | $\Delta \bar{H}_s$, kcal/mole |
|---|---|---|---|---|---|
| ODTB | 27.21 | 20.46 | 12 | −23.1 ± 0.4 | ... |
| ODTB | 18.14 | 13.59 | 3 | −21.8 ± 0.2 | ... |
| ODTB | 9.07 | 6.80 | 3 | −22.0 ± 0.3 | ... |
| ODTB | 1.06 | 0.80 | 6 | −20.4 ± 0.2 | ... |
| ODTB | 0.00 | 0.00 | Extrap | −20.4 ± 0.2 | ... |
| PDTB | 27.21 | 20.46 | 18 | +7.8 ± 0.4 | ... |
| PDTB | 18.14 | 13.80 | 4 | +8.2 ± 0.4 | ... |
| PDTB | 9.07 | 6.83 | 4 | +8.9 ± 0.5 | ... |
| PDTB | 1.06 | 0.80 | 5 | +9.2 ± 0.4 | ... |
| PDTB | 0.00 | 0.00 | Extrap | +9.2 ± 0.2 | ... |
| MDTB | 1.06 | 0.80 | 3 | +0.9 ± 0.3 | ... |
| ODTB | 0.00 | 0.00 | 7 | ... | +0.7 ± 0.2 |
| PDTB | 0.00 | 0.00 | 8 | ... | +8.1 ± 0.4 |
| MDTB | 0.00 | 0.00 | 3 | ... | +0.8 ± 0.2 |
| 124-TTB | 5.77 | 4.93 | 2 | −13.9 ± 0.4 | ... |
| 135-TTB | 5.77 | 4.92 | 2 | +5.5 ± 0.2 | ... |
| 124-TTB | 4.22 | 12.4 | 1 | −8.2 | ... |
| 135-TTB | 4.22 | 12.2 | 2 | +10.3 ± 0.6 | ... |
| 124-TTB | 4.22 | 3.61 | 1 | −14.1 | ... |
| 135-TTB | 4.22 | 3.64 | 1 | +5.2 | ... |
| 124-TTB | 0.00 | 0.00 | 2 | ... | +8.8 ± 1.0 |
| 135-TTB | 0.00 | 0.00 | 2 | ... | +5.6 ± 0.8 |

tripled without having to prepare and maintain more catalyst stock solutions. A statistical analysis of the results obtained on first, second, and third injections by means of Student's t test[47] indicated that there was less than one chance out of a hundred that the $\Delta H_{\text{obsd}}$ or $\Delta \bar{H}_s$ of any injection was affected by its order of addition in pure carbon disulfide or $27.21 \times 10^{-3}$ *M* aluminum bromide. Therefore, the concentrations of products from one injection into this concentration of catalyst were too small to affect the heat terms for the next injection. Pooling of consecutive measurements in the same catalyst system was not possible, however, at lower concentrations. This is why the statistical samples for $\Delta H_{\text{obsd}}$ in them are smaller. Since $\Delta H_{\text{obsd}}$ for all aromatics is dependent upon the [$\text{AlBr}_3$], extrapolations to zero catalyst concentration were made in all cases where sufficient data permitted. This was accomplished through a least-squares calculation by use of $\Delta H_{\text{obsd}}$ and [$\text{AlBr}_3$]/[aromatic] as variables. Before pooling the data at different concentrations in this way, it was first established through the F test[47] that the precision of data under different reaction conditions was comparable. The standard deviation of $\Delta H_{\text{obsd}}$ values for ODTB and PDTB were shown to be compatible below the critical 5% level. We were unable to make such a valid comparison for MDTB because of the small statistical sample of data occasioned by a short supply of this compound. Least-squares treatment of these data gave for ODTB an intercept for $\Delta H_{\text{obsd}}$ at [$\text{AlBr}_3$] = 0 of −20.43 ± 0.17 kcal/mole with a standard deviation for $\Delta H_{\text{obsd}}$ in the pooled data of ±0.45 kcal/mole. The slope of the least-squares line was −0.129 ± 0.011. For PDTB, the least-squares intercept was +9.22 ± 0.15, SD of a single measurement ±0.40, and the slope was −0.0693 ± 0.0092. The most important facts to emerge are, first, that within experimental error, the change in total heat of reaction for ODTB from $27 \times 10^{-3}$ *M* aluminum bromide to [$\text{AlBr}_3$] = 0 corresponds exactly to that change for PDTB; and secondly, that $\Delta H$ of total reaction for MDTB agrees within experimental error with that for PDTB.

The strain energy for ODTB is defined (see section 6 below) by the equation

$$\Delta H^\circ_{\text{strain}}(\text{ODTB}) = [\Delta H_{\text{rx}}(\text{ODTB}) - \Delta H_{\text{rx}}(\text{PDTB})] \quad (1)$$

where

$$\Delta H_{\text{rx}}(\text{aromatic}) = \Delta H_{\text{obsd}}(\text{aromatic}) - \Delta \bar{H}_s(\text{aromatic})$$

Values of the strain energy were derived from the data in Table IV at different [$\text{AlBr}_3$]. Standard deviations in each case were taken by a linear combination of the variances[48] for $\Delta H_{\text{obsd}}$ and $\Delta \bar{H}_s$ for the strained and unstrained molecules in each case. They are presented in Table V where $\Delta H_{\text{strain}}$ for ODTB based on both *p*- and *m*-di-*t*-butylbenzene as models is seen to be invariant to [$\text{AlBr}_3$]. The slight discrepancy involving MDTB may be assigned either to experimental error as a result of a small statistical sample for this compound or to possible unsymmetrical buttressing of the bulky 1,3-di-*t*-butyl groups relative to the *para* isomer.

**Table V.** Strain Energy of *o*-Di-*t*-butylbenzene

| $10^3[\text{AlBr}_3]$, moles/l. | $10^3$[aromatic], moles/l. | Model compd | $\Delta H_{\text{strain}}$(ODTB), kcal/mole |
|---|---|---|---|
| 27.21 | 1.28–1.35 | PDTB | −23.4 ± 0.7 |
| 18.14 | 1.28–1.35 | PDTB | −22.7 ± 0.6 |
| 9.07 | 1.28–1.35 | PDTB | −23.5 ± 0.7 |
| 1.06 | 1.28–1.35 | PDTB | −22.1 ± 0.7 |
| 1.06 | 1.28–1.35 | MDTB | −21.1 ± 0.5 |
| 0.00 | 1.28–1.35 | PDTB | −22.3 ± 0.5 |

**6. Relation of Measured Values to the Strain Energy.** Measured values are related to $\Delta H_{\text{strain}}$ by the following cycle for conversion of the aromatic compound (Ar) to products (P).

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(47) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

(48) O. L. Davies, Ed., "Statistical Methods in Research and Production," Hafner Publishing Co., New York, N. Y., 1957.

The meanings of the various heat terms are as follows, all processes referring to a mole at 30°.

I. $\Delta H^\circ_{\mathrm{rx}}(\mathrm{g})$ is the standard enthalpy for conversion of a mole of Ar as an ideal gas to a corresponding mole of the isomerization products (P) under the same conditions.

II. $\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}}$ is the enthalpy change for condensing the mole of Ar to itself as pure liquid or solid. This corresponds to the heat of vaporization or sublimation with its sign changed.

III. $\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}}$ is the partial molar heat of solution for Ar in $\mathrm{CS_2}$. This value is measured in $\mathrm{CS_2}$ and it is assumed that small quantities of aluminum bromide would have no effect on it were it not for complexing (see IV).

IV. $\Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}}$ is the hypothetical heat of complexing of Ar with all acids such as $\mathrm{AlBr_3}$, HBr, $\mathrm{HAlBr_4}$ after dissolving in the catalyst solution and prior to reaction.

V. $\Delta H_{\mathrm{rx}}$ is the heat of reaction of complexed Ar to complexed products $\mathrm{P{\cdot}AlBr_3}$.

VI, VII, and VIII correspond to the reverse of processes IV, III, and II and they apply to P rather than to Ar.

$\Delta H_{\mathrm{obsd}}$, the molar heat which is actually measured for injection of an increment of ODTB into a carbon disulfide solution of aluminum bromide, is, therefore, given by

$$\Delta H_{\mathrm{obsd}} = \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}} + \Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}} + \Delta H_{\mathrm{rx}} \qquad (2)$$

The complete equation for the hypothetical gas phase conversion of Ar to products P is

$$\Delta H^\circ_{\mathrm{rx}}(\mathrm{g}) = \Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}} + \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}} + \Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}} + \Delta H_{\mathrm{rx}} - \Delta H^{\mathrm{P}}{}_{\mathrm{comp}} - \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{P}} - \Delta H^{\mathrm{P}}{}_{\mathrm{vap}} \qquad (3)$$

If Ar corresponds to a strained aromatic and Ar′ is its unstrained isomer which gives an identical product mixture, a similar cycle and equation may be written for the latter. Subtracting the equation for Ar′ from that for Ar, one then obtains (using primes throughout to refer to the unstrained isomer) the following

$$\Delta H^\circ_{\mathrm{rx}}(\mathrm{g}) - \Delta H^\circ_{\mathrm{rx}}{}'(\mathrm{g}) = (\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}} - \Delta H^{\mathrm{Ar}'}{}_{\mathrm{cond}}) + (\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}} - \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}'}) + (\Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}} - \Delta H^{\mathrm{Ar}'}{}_{\mathrm{comp}}) + (\Delta H_{\mathrm{rx}} - \Delta H'_{\mathrm{rx}}) \qquad (4)$$

since all terms for the products vanish if they are formed in equal amounts from Ar and Ar′. It will be shown below that to a good approximation (±1 kcal/mole) the sum of the first three terms on the right of eq 4 is negligible, in which case the difference between the heats of reaction for Ar and Ar′ in solution is equal to that in the gas phase at the same temperature. Now, in the gas phase for the conversion of 1 mole of Ar to 1 mole of P

$$\Delta H^\circ_{\mathrm{rx}}(\mathrm{g}) = \Delta H_{\mathrm{f}}(\mathrm{Ar}) - \Delta H_{\mathrm{f}}(\mathrm{P})$$

and if

$$\Delta H^\circ_{\mathrm{rx}}{}'(\mathrm{g}) = \Delta H_{\mathrm{f}}(\mathrm{Ar}') - \Delta H_{\mathrm{f}}(\mathrm{P})$$

then

$$\Delta H^\circ_{\mathrm{rx}}(\mathrm{g}) - \Delta H^\circ_{\mathrm{rx}}{}'(\mathrm{g}) = \Delta H_{\mathrm{f}}(\mathrm{Ar}) - \Delta H_{\mathrm{f}}(\mathrm{Ar}')$$

which difference corresponds to "strain energy" as we have defined it. We must now justify cancellation of the first three terms on the right.

$$\begin{tikzcd}
\mathrm{Ar(g)} \arrow[r, "\Delta H^\circ_{\mathrm{rx}}(\mathrm{g})", "\mathrm{I}"'] \arrow[d, "\Delta H^{\mathrm{Ar}}_{\mathrm{cond}}", "\mathrm{II}"'] & \mathrm{P(g)} \\
\mathrm{Ar(pure)} \arrow[d, "\Delta \bar{H}_{\mathrm{s}}^{\mathrm{Ar}}", "\mathrm{III}"'] \arrow[rdd, "\Delta H_{\mathrm{obsd}}"] & \mathrm{P(pure)} \arrow[u, "\mathrm{VIII}", "-\Delta H^{\mathrm{P}}_{\mathrm{cond}}"'] \\
\mathrm{Ar(CS_2)} \arrow[d, "\Delta H^{\mathrm{Ar}}_{\mathrm{comp}}", "\mathrm{IV}"'] & \mathrm{P(CS_2)} \arrow[u, "\mathrm{VII}", "-\Delta \bar{H}_{\mathrm{s}}^{\mathrm{P}}"'] \\
\mathrm{Ar{\cdot}AlBr_3} \arrow[r, "\Delta H_{\mathrm{rx}}", "\mathrm{V}"'] & \mathrm{P{\cdot}AlBr_3} \arrow[u, "\mathrm{VI}", "-\Delta H^{\mathrm{P}}_{\mathrm{comp}}"']
\end{tikzcd}$$

Figure 1. Enthalpy cycle.

**7. Justification of Assumptions.** For isomeric, liquid dialkylbenzenes[49–51] (dimethyl-, methylethyl-, diethyl-, methyl-*n*-propyl-, methylisopropylbenzenes and the methylstyrenes), the heats of vaporization agree for all *ortho–meta* pairs within 0.2 kcal/mole and for *ortho–para* pairs within 0.3 kcal/mole. In all cases, the value for the *ortho* isomer is about 0.2 kcal/mole more endothermic than for the other two isomers, perhaps reflecting small differences in dipole–dipole attractions. $\Delta H_{\mathrm{vap}}$ for 1,2,4- and 1,3,5-trimethylbenzenes agree within 0.15 kcal/mole, as also do the corresponding dimethylethylbenzenes.[51] Therefore, we are justified in assuming that $(\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}} - \Delta H^{\mathrm{Ar}'}{}_{\mathrm{cond}}) \approx 0$ for isomeric, *liquid* benzenes.

There are very few published data to support or refute the assumption that $(\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}} - \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}'}) \approx 0$, although one would surely expect arenes to form relatively perfect solutions so that except for crystalline ones $\Delta \bar{H}_{\mathrm{s}} \approx 0$ in carbon disulfide. Differences between them would be especially small. The most direct datum in this case is from Table IV where it is seen that $(\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{ODTB}} - \Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{MBTD}}) = 0$ within experimental error. We find quite generally that other molecules of similar size and polarity also give equal $\Delta \bar{H}_{\mathrm{s}}$ from a pure liquid standard state to high dilution in most solvents (water being a notable exception). Thus, *t*-butyl and *n*-butyl chloride agree with each other and with isopropyl bromide within 0.3 kcal/mole in 50% aqueous ethanol.[43]

Several of the aromatics in this study are solids at 30°. For them, large and unpredictable lattice energies complicate the relatively small and systematic trends in $\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}}$ or $\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}}$ which result from separating the hydrocarbon molecules from each other in the pure crystal to high attenuation as a gas or dilute solution in $\mathrm{CS_2}$. However, the lattice energy term will make equal and opposite heat of fusion contributions to $\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}}$ and to $\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}}$ (heat of sublimation). The rest of $\Delta H^{\mathrm{Ar}}{}_{\mathrm{cond}}$ or $\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}}$ would be the same as if the liquid compound were used.[52] Since $\Delta \bar{H}_{\mathrm{s}}{}^{\mathrm{Ar}}$ was measured independently for each compound and subtracted from the total molar heat accompanying injection of Ar into the catalyst solution, the only remaining terms are those for $\Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}}$ and $\Delta H^{\mathrm{Ar}}{}_{\mathrm{rx}}$.

That $(\Delta H^{\mathrm{Ar}}{}_{\mathrm{comp}} - \Delta H^{\mathrm{Ar}'}{}_{\mathrm{comp}}) \approx 0$ is suggested by the facts that $\Delta H_{\mathrm{obsd}}$ for individual compounds is rather

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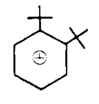
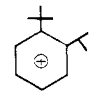
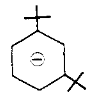
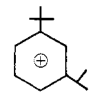
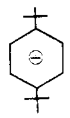
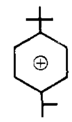
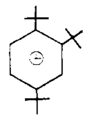
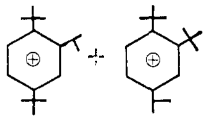
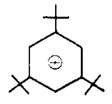
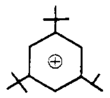
(49) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).

(50) H. E. Clements, K. V. Wise, and S. E. J. Johnson, *ibid.*, **75**, 1593 (1953).

(51) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 455 (1946).

(52) On the assumption that the only difference between $\Delta \bar{H}_{\mathrm{s}}$ for crystalline PDTB and liquid ODTB or MDTB is the heat of fusion of the former, $\Delta H_{\mathrm{fusion}}(\mathrm{PDTB},30°)$ can be calculated as +7.4 kcal/mole.

**Table VI.** Mass Spectral Estimation of Strain Energy

| | Ionization potential ($IP$) of parent hydrocarbon, ev | P − 15 appearance potential ($AP$, ev) ($AP$ − $IP$) = Δ | | Strain energy = $\Delta_{\text{strained}} - \Delta_{\text{unstrained}}$ |
|---|---|---|---|---|
| 1 | <br>$IP$ = 8.60 | <br>P − 15<br>$AP$ = 10.64 | $\Delta_1$ = 2.04 ev | |
| 2 | <br>$IP$ = 8.71 | <br>P − 15<br>$AP$ = 11.70 | $\Delta_2$ = 2.99 ev | $\Delta_1 - \Delta_2$ = −0.95 ev = −22 kcal/mole |
| 3 | <br>$IP$ = 8.74 | <br>P − 15<br>$AP$ = 11.69 | $\Delta_3$ = 2.95 ev | $\Delta_1 - \Delta_3$ = −0.91 ev = −21 kcal/mole |
| 4 | <br>$IP$ = 8.60 | <br>$P$ − 15<br>$A$P = 11.14 | $\Delta_4$ = 2.54 ev | $\Delta_4 - \Delta_5$ = −0.81 ev = −19 kcal/mole |
| 5 | <br>$IP$ = 8.56 | <br>P − 15<br>$AP$ = 11.91 | $\Delta_5$ = 3.35 ev | |

insensitive to large changes in [$AlBr_3$] so that ($\Delta H^{\text{Ar}}{}_{\text{obsd}} - \Delta H^{\text{Ar}'}{}_{\text{obsd}}$) is nearly constant for isomeric di- and tri-*t*-butylbenzenes described herein. The assumption is supported by several thermodynamic studies of aromatic complexes[53] with HBr,[54] $AlBr_3$,[55] HF,[56] and $HSO_3F$[57] which show that $\Delta H^{\text{Ar}}{}_{\text{comp}}$ is relatively insensitive to minor structural variation and is usually rather small.[58] Even for the solid [aromatic]·[$AlBr_3$]$_2$ type of complex which is formed relatively exothermically,[55] there is a difference of only 1.8 kcal/mole between benzene and mesitylene, and the three xylenes agree within 1 kcal/mole.[59] The validity of this assumption is also important for cases where identical products are not formed. If there were wide differences of $\Delta H_{\text{comp}}$ for different aromatic products, the treatment used here would break down seriously.

8. **Appearance Potentials.** Using an A.E.I. MS9 mass spectrometer at Mellon Institute, Dr. Michael Barber, of Associated Electrical Industries International, Ltd., determined the values shown in Table VI for the ionization potentials of the molecules and the appearance potentials of P − 15 fragments. A special slow drive scanning motor was used to increase the voltage smoothly and continuously so that direct evaporation of the compounds could be made into the ion chamber. The scan times were made sufficiently short to overcome sample pressure changes. Experimental error was shown to be ±0.07 ev.

If one accepts the assignments shown in Table VI, the appearance potentials are interpretable as giving rough support to our values from solution calorimetry, the average strain energy by this method of mass spectral analysis being 20.7 ± 2 kcal/mole. The weak points of the argument are the usual ones of mass spectrometry, firstly, that of making gross structural assignments to the ions associated with each mass peak, and secondly, the assumption that the energy–geometry relationships for the "strained" and "unstrained" ion are relevant to the reactions occurring in solution. The strong point is the fact that although the first ionization potentials of isomeric strained and unstrained di- and tri-*t*-butylbenzenes are nearly the same, there are large differences between strained and unstrained isomers in the appearance potentials for P − 15 peaks. The energy differences correspond closely with the calorimetric strain energies.

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(53) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 104.

(54) H. C. Brown and J. J. Melchiore, *J. Am. Chem. Soc.*, **87**, 5269 (1965).

(55) S. U. Choi and H. C. Brown, *ibid.*, **88**, 903 (1966).

(56) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

(57) J. Larsen, unpublished results.

(58) For reviews on base strengths of aromatic hydrocarbons, see ref 44, 53, and (a) H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 195 (1966); (b) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963); (c) D. A. McCaulay and A. P. Lien in "Conference on Hyperconjugation," V. J. Shiner, Jr., and E. Campaigne, Conference Cochairmen, Pergamon Press, Inc., New York, N. Y., 1959.

(59) This probably corresponds to the experimental error (although none was given) of these measurements since they were obtained at low temperature by the van't Hoff method.

**Table VII.** Standard Heats of Formation[51] of Isomeric Di- and Trialkylbenzenes at 25°

| Compound | $\Delta H_f°$, kcal/mole; gas phase |  |  | $\Delta\Delta H_f°$, kcal/mole |  |
|---|---|---|---|---|---|
|  | *ortho* | *meta* | *para* | *ortho* − *meta* | *ortho* − *para* |
| Xylene | +4.54 ± 0.26 | +4.12 ± 0.18 | +4.29 ± 0.24 | +0.42 ± 0.44 | +0.25 ± 0.50 |
| Methylethylbenzene | +0.29 ± 0.28 | −0.46 ± 0.29 | −0.78 ± 0.35 | +0.75 ± 0.57 | +1.07 ± 0.63 |
| Diethylbenzene | −4.53 ± 0.40 | −5.22 ± 0.40 | −5.32 ± 0.40 | +0.69 ± 0.80 | +0.79 ± 0.80 |
| Methyl-*n*-propylbenzene | −5.17 ± 0.50 | −5.86 ± 0.50 | −5.97 ± 0.50 | +0.69 ± 1.00 | +0.80 ± 1.00 |
| Methylisopropylbenzene | −6.10 ± 0.50 | −6.79 ± 0.50 | −6.90 ± 0.50 | +0.69 ± 1.00 | +0.80 ± 1.00 |
| Trimethylbenzene | −3.33 ± 0.27[a] | −3.84 ± 0.34[b] |  |  |  |
| Dimethylethylbenzene | −7.91 ± 0.60[c] | −8.50 ± 0.60[d] |  |  |  |

[a] 1,2,4. [b] 1,3,5. [c] 1,2-Dimethyl-4-ethyl-. [d] 1,3-Dimethyl-5-ethyl-.

## Discussion

We have defined the strain energy ($\Delta H°_{\text{strain}}$) in two *o*-di-*t*-butylbenzene systems (ODTB and 124-TTB) as being the difference between the standard heats of formation from elemental carbon and hydrogen in the gas phase at 30° ($\Delta H_f°$) for these compounds and their unstrained isomers (PDTB or MDTB and 135-TTB, respectively). This is equivalent to saying that in both the di- and tri-*t*-butylbenzene series, there would be no energy difference between isomers were it not for the steric interaction of the *o*-*t*-butyl groups. Justification for this assumption is provided by the data presented in Table VII showing that in all cases,[51,60,61] there is no difference in $\Delta H_f°$ within experimental error between di- and trialkylbenzene position isomers bearing "small" alkyl groups.

ODTB and 124-TTB are completely isomerized within several seconds by dilute solutions of aluminum bromide in carbon disulfide through reactions which are enormously exothermic relative to those of the unstrained isomers. Careful comparison of product mixtures shows that in every case the strained and unstrained isomers give essentially the same array of products ranging from 2 or 4 at low [$AlBr_3$] to over 37 at higher [$AlBr_3$]. Despite the fact that the yields of products and heats of reaction are quite sensitive to conditions, *the results show unmistakeably that there is a single unvarying difference of 22.3 kcal/mole between strained and unstrained isomers.* This difference is not only invariant to conditions and to wide changes in reaction stoichiometry, it is identical for both the di-*t*-butylbenzene ($\Delta H_{\text{strain}} = 22.3 \pm 0.5$ kcal/mole) and tri-*t*-butylbenzene ($\Delta H_{\text{strain}} = 22.3 \pm 1.0$ kcal/mole) series. Furthermore, a similar difference (*ca.* 20 kcal/mole) can be assigned to appearance potentials for appropriate fragments in the mass spectra of these compounds. Taken together, these results present an overwhelming case for our thesis that the strain energy in *o*-di-*t*-butylbenzenes is indeed close to 22 kcal/mole.

We have related the difference in heat of reaction in solution between strained and unstrained di- and tri-*t*-butylbenzenes by assuming that for isomeric pairs the heats of transfer from gas phase to solution are equal and that the same is true for their heats of complexing. Each of our four basic assumptions[62] may be justified within an experimental error of 0–1 kcal/mole. Their cumulative error taken at its largest could scarcely exceed ±2 kcal/mole which is less than 10% of the value we wish to define. In view of discrepancies of over 100% between previous possibilities for this figure, we feel that high precision is relatively unimportant here compared to the rough accuracy which we claim for our figure. It is agreed by all workers on this problem that a large energy term is associated with the *o*-di-*t*-butyl interaction. In general, accuracy is much more important and difficult to obtain than precision for physicochemical measurements. Furthermore, since organic molecules are too large and complex for rigorous interpretation of structure–reactivity behavior, *it is generally true that a rough proportionality holds between the size of a reactivity effect and our ability to relate it to a single structural change.*[63] Thus, although the present result is of only moderate precision, we consider it to be of value because its accuracy is supported by several independent lines of evidence and the energy difference between strained and unstrained isomers is so large that it can be related unequivocally to the *ortho*-steric interaction.

**Reconciliation with a Previous Result.** Of the various estimates of the strain energy in the *o*-di-*t*-butyl system, only one previous measurement has employed a compound actually incorporating this structural feature; the others are based on more or less appropriate analogs because they predated the first synthesis of a *bona fide* *o*-di-*t*-butyl hydrocarbon (124-TTB) by Hübel's group in 1961.[25] Hübel reports measurements by Fischer and Reckziegel of the difference in heat of combustion between 124- and 135-TTB to be −16.8 ± 1.7 kcal/mole. This value, however, makes no allowance for possible differences in the heat of sublimation (required to convert the two solids to gas prior to burning), which may be quite substantial[35] in systems of this kind. If one assigns all of the difference in $\Delta \bar{H}_s$ for the two crystalline isomers into carbon disulfide to the heat of fusion,[64] the data in Table IV indicate that the heat of sublimation of the 1,2,4 isomer is 3.2 ± 1.8 kcal/mole more endothermic than the 1,3,5. Added to Fischer and Reckziegel's figure, this gives a difference of 20 ± 2 kcal/mole between the isomers agreeing within combined experimental error with our value.

Although correspondence of our result with Brown's[4–7] original estimate is in part fortuitous, it must surely be taken as strong support for the method of homomorphic analogy in view of the fact that the present case is one of his most extreme applications of it.

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(60) A minor exception is the methylethylbenzenes where *ortho–meta* and *ortho–para* differences are slightly outside experimental error.

(61) In every case, the *ortho* or 1,2,4 isomer is slightly more energy rich than are other isomers, but the trend is within experimental error.[60] Since the *ortho–para,meta* difference shows some sensitivity to the size of the groups, even this small trend probably reflects steric compression.

(62) (a) $\Delta H_{\text{strain}} = \Delta H_f°(\text{Ar}) - \Delta H_f°(\text{Ar}')$. (b) $\Delta\Delta H$ of transfer from gas to $CS_2$ = 0. (c) $\Delta\Delta H_{\text{comp}} = 0$. (d) Product mixtures from Ar and Ar′ are exactly identical.

(63) J. R. Platt, *Science*, 146, 347 (1964).

(64) See Justification of Assumptions section.

**Physicochemical Consequences of the Strain.** We have shown that *o*-di-*t*-butylbenzenes carry a steric strain which is over half of the generally accepted resonance energy of benzene. We shall now consider what, if any, evidence exists for partial loss of "aromatic character" in such compounds in order to accommodate this strain.

"Aromatic character" or "aromaticity" are defined operationally by too many facts about too many compounds to be identified neatly through any single experimental criterion, although they may be defined conceptually in a variety of ways.[65] We shall look for manifestations of decreased aromaticity in the present case in two sets of properties: (a) those that essentially represent the unperturbed ground state, and (b) those that are expressed by reactivity properties where the molecule goes from its ground state to an energetically excited state.

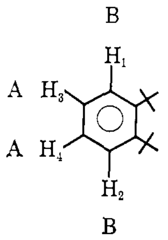
**Ground-State Properties.** Response to an external magnetic field produces only a minor perturbation of a diamagnetic molecule. It has been suggested[65,66] that the exaltation of diamagnetic susceptiblilty is an especially important criterion for the degree of aromatic character. Dauben, using Haberditzl's revised Pascal constants, has determined these values for the *t*-butylbenzenes considered in this paper.[67] He finds that benzene, TB, PDTB, and 135-TTBB, the unstrained compounds, have the same exaltation within experimental error. However, ODTB has 71 ± 2% of the "fully aromatic" value and 124-TTBB has 69 ± 7%. These are large effects on this property and constitute *the strongest evidence of which we are presently aware that the aromatic $\pi$-electron* system has been appreciably influenced by the presence of an *o*-di-*t*-butyl grouping.

One might suppose that disruption of the benzene ring current would influence the chemical shifts and coupling constants for ring protons in the above series of compounds. Measurements by Bothner-By[68] (Table VIII) and Castellano[68] and Gibbons and Gil[69] show that the effect, if it exists, is small.

These values are mostly normal for *ortho*-disubstituted aromatic compounds. However, $J_{3,4}$ is the lowest yet observed[70] for an *ortho*-disubstituted benzene and may reflect an abnormal bond length. We also find the ring protons of highly strained 1,2,3,5-tetra-*t*-butylbenzene lie upfield at $\tau$ 3.07 ppm,[71] compared to which those of its 1,2,4,5 isomer are at 2.57 ppm like the B protons of ODTB. In contrast, the chemical shifts for methyl protons in the *t*-butyl groups are invariably displaced downfield by about 0.20 ppm,[30,31,36,69] presumably because of dispersion forces.

For the most part, the infrared spectra of strained and unstrained poly-*t*-butylbenzenes show no striking differences. However, Dale[72] and Hübel[27] suggested that the spectra of 124-TTB and 1,2,4,5-tetra-*t*-butylbenzene could be interpreted as evidence for warping of the ring particularly on the basis of the band at 1585 cm$^{-1}$. Since numerous other unstrained *t*-butylbenzenes also give a sharp band in this region, the argument is not conclusive.

**Table VIII.** Complete Analysis of Proton Magnetic Resonance of ODTB in Solution

| | Coupling constants, cps | Chemical shifts, ppm |
|---|---|---|
|  | $J_{1,3} = J_{2,4} =$ 8.1[a]<br>8.11[b]<br>$J_{1,4} = J_{2,3} =$ 1.7[a]<br>1.59[b]<br>$J_{1,2} =$ 0.2[a]<br>0.27[b]<br>$J_{3,4} =$ 7.1[a]<br>7.00[b] | A protons, $\tau$ 3.68[68]<br>3.02,[69] 3.028[68b]<br>B protons, $\tau$ 3.17[68]<br>2.57,[69] 2.554[68b] |

[a] 50% in carbon tetrachloride. [b] 10% in carbon tetrachloride.

Independent evidence for severe warping of 1,2,4,5-tetra-*t*-butylbenzene into a boat-shaped form would be provided if it had a dipole moment. Dr. N. L. Allinger of Wayne State University[73] has measured this carefully and finds $\mu < 0.3$ D. (*i.e.*, immeasurably small).

So far, to our knowledge, no molecular structure analysis of an *o*-di-*t*-butylbenzene system has been achieved by X-ray or electron diffraction.[74]

**Reactivity and Electronic Spectral Properties.** The physical properties of molecules in their ground states are of chemical interest chiefly because of any light they may throw on the ability of the molecule to go to a higher energy state by absorption of kinetic or electromagnetic energy. Comparison of two compounds (*e.g.*, ODTB and PDTB) by equilibria, kinetics, or electronic spectra has the inherent complication of involving four states, two initial states and two secondary states (products, transition states, or excited states). In the present instance, it is remarkable to find few chemical or spectral manifestations of the enormous energy difference between the molecules. This is most likely because there is very little relief of strain in the ODTB system when passing to many of the transition or excited states that might be used for comparison.

By far the largest thermodynamic and kinetic effect that is produced on a thermal reaction of the ODTB system is that which we have exploited here in order to determine the strain energy.

A Lewis acid can withdraw $\pi$ electrons between the *o*-*t*-butyl groups from involvement in aromatic delocalization to form the type II cation shown below which must be close to the transition state for de-*t*-butylation. Once formed, this intermediate can release the tremendous energy of the *o*-di-*t*-butyl interaction in

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(65) D. P. Craig in "Nonbenzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter I.

(66) H. Dauben, Benzene Centennial Symposium, 150th National Meeting of the American Chemical Society, Sept 1965; see also W. Haberditzl, *Angew. Chem.*, **78**, 277 (1966).

(67) H. Dauben, private communication. We are very grateful to Professor Dauben for communicating these results to us.

(68) A. A. Bothner-By and S. M. Castellano, private communication. We wish to express our appreciation to Professors Bothner-By and Castellano for duplicate complete analyses of the $A_2B_2$ spectrum using the LAOCOON program at Mellon Institute.

(69) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 163, 167 (1965).

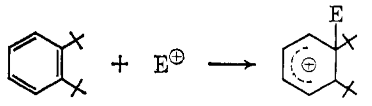
(70) A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965).

(71) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(72) J. Dale, *Chem. Ber.*, **94**, 2821 (1961).

(73) We greatly appreciate Professor Allinger's measurement of this property. This experiment was originally suggested by Professor N. LeBel.

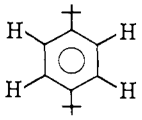
(74) NOTE ADDED IN PROOF. Professor C. H. Stam has sent the results of a refined X-ray analysis of 1,2,4,5-tetra-*t*-butylbenzene, which show this ring to be planar. The strain is mainly relieved by bending adjacent *t*-butyl groups away from each other in the plane of the ring. We are very grateful to Professor Stam for permission to report these results.



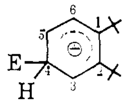
I II

a single exothermic and, therefore,[75] very fast step. The formation of the equivalent cation in the *p*-di-*t*-butylbenzene system has no special driving force for loss of the *t*-butyl group.

In both ODTB and PDTB, there are strong and nearly equal steric factors which militate against attack of an electrophile on a carbon bearing a *t*-butyl group. In PDTB, steric hindrance on the other ring positions must also be severe so that all ring carbons are protected, being attached directly to a *t*-butyl *group* or being *ortho* to one.



III



IV

On purely steric grounds then, the 4 and 5 positions of ODTB are greatly favored for attack over its 1 and 2 positions or the 1 and 4 carbons of PDTB. The 3 and 6 positions of ODTB are sterically equivalent to the 2, 3, 5, and 6 positions of PDTB.

There are also potent electronic factors which favor initial attack on ring carbons bearing hydrogen in both strained and unstrained isomers. It is a well-known fact that aryl cations such as IV enjoy considerable stabilization from their alkyl groups[36,38] relative to aryl cations with only hydrogen or ring carbons to which positive charge is transmitted. Therefore, the complexes formed by *o*-, *m*-, and *p*-dialkylbenzenes are electronically of comparable stability and are most favorably formed when the electrophile attacks a position *ortho* or *para* to an alkyl group.[76]

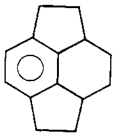
The reactions of ODTB are consistent with these effects. Nitration gives attack at the 4 and 5 positions somewhat in preference to the 3 or 6 ones,[36,77] as also does Friedel–Crafts acylation.[36] In the latter reaction, dislodgement of a *t*-butyl group competes with displacement of ring hydrogen. Both ODTB and PDTB (see Experimental Section) are attacked vigorously by Hart's reagent (peroxytrifluoroacetic acid and boron trifluoride), but both are impervious to $BF_3$ alone under the same conditions. Bromination without di-*t*-butylation occurs slowly in acetic acid,[36] but again loss of a *t*-butyl group may accompany introduction of iron powder to produce Friedel–Crafts catalyst. The only kinetic comparison[78,79] of which we are aware is a preliminary rate study indicating that ODTB undergoes uncatalyzed bromination about ten times faster than PDTB.[78]

Bulky electrophiles such as $Br_2$, $NO_2^+$, and $BF_3$, therefore, show little tendency to attack carbons bearing *t*-butyl groups. With these reagents, ODTB and PDTB are of comparable reactivity, the unhindered 4 and 5 positions of ODTB being favored slightly. Smaller, strongly acidic electrophiles such as $HAlBr_4$, $OH^+$, are better able to produce type II cations and instantly lose the *t*-butyl group from the *ortho* position. This step is so fast that whenever this route is feasible, ODTB may be removed rapidly through it even though the formation constant for type II cations be very favorable. *The strain energy in ODTB may be likened to that which is stored in the spring of a large and well-shielded bear trap: an enormous driving force is available, but only through proper activation of the trigger.*

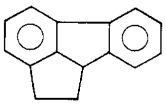
The most dramatic new chemistry to be derived from the study of *o*-di-*t*-butylbenzenes is their photolysis to valence isomers of benzene. Apparently, this was approached originally by van Tamelen and Pappas[80] to take advantage of the strain energy in 124-TTB. In view of the fact that a number of such isomers have been made photolytically without assistance from ground-state strain energy and others have been formed by remarkable nonphotolytic cyclization reactions, it is now clear that ring strain is not an important requirement for these tranformations.[81–84]

ODTB may be compared to two other strained aromatic systems. [2.2]Paracyclophane[22,23] is shown by X-ray analysis[85] to have normal bond lengths, although the rings are puckered. Its heat of combustion[86] suggests a strain energy of 31 kcal/mole relative to a linear hypothetical unstrained model (Franklin's method). It undergoes normal aromatic ring nitration, but may be isomerized to less strained products by photolysis or treatment with HCl and $AlCl_3$.

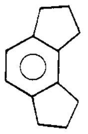
Rapoport's group[19–21,87] reports that V and VI have



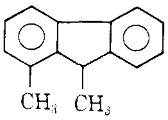
V



VI



VII



VIII

pronounced olefinic activity, being readily attacked by atmospheric oxygen, perbenzoic acid at room temperature, and hydrogen with palladized carbon. These properties are in sharp contrast to VII, VIII, ODTB, [2.2]-paracyclophane, and all other strained aromatics of which we are aware. V and VI, therefore, are the only extant examples of benzenes in which loss of aromatic character has been induced by ring strain. No X-ray

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(75) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(76) Extreme warping of the benzene ring in ODTB to relieve strain should localize electrons in positions away from the 1,2 bond and also reduce $-CCH_3$ hyperconjugative stabilization by bending the *t*-butyl groups out of the ring plane.

(77) B. Van de Graff and B. M. Webster, *Rec. Trav. Chim.*, **85**, 619 (1966).

(78) See thesis of J. C. S. In 80% aqueous acetic acid containing 0.20 *M* NaBr at 80°, ODTB reacts with bromine, $k_2 = 20.5 \pm 1.1 \times 10^{-3}$ l. mole$^{-1}$ sec$^{-1}$, compared to $k_2 = 1.89 \pm 0.05 \times 10^{-3}$ l. mole$^{-1}$ sec$^{-1}$ for PDTB. Both substrates follow second-order kinetics to over three half-lives.

(79) In the early phases of this work, the possibility arose that bond fixation might occur in ODTB which could engender carcinogenic properties.[18] A careful screening study by Dr. William Poel of the University of Pittsburgh showed no tendency toward development of malignancies in mice injected with ODTB or PDTB.

(80) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

(81) See E. E. van Tamelen, *Angew. Chem. Intern. Ed. Engl.*, **4**, 738 (1965), and H. G. Viehe, *ibid.*, **4**, 746 (1965), for excellent reviews of these fields, and ref 82–84.

(82) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).

(83) D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966).

(84) R. Criegee and R. Askani, *Angew. Chem. Intern. Ed. Engl.*, **5**, 519 (1966).

(85) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(86) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966).

(87) J. Z. Pasky, Ph.D. Thesis, University of California, Berkeley, Calif., 1956.

analysis has been reported for V, but its strain energy has been estimated[87] as 46 kcal/mole.

**Electronic Spectra.** The only marked effect of ring strain on the ultraviolet spectra of *o*-di-*t*-butylbenzene systems is a loss of intensity and vibrational fine structure of the secondary bands between 240 and 280 mμ.[25–31,36] Only when three *t*-butyl groups are juxtaposed[88,89] are large bathochromic shifts comparable to those seen in [2.2]paracyclophane and compound V observed. Assuming that equivalent assignments may be made for the bands in strained and unstrained isomers, these results simply indicate that little or no strain energy is released on going to the excited state. There are so many reasonable but unverifiable interpretations of this fact that discussion at this time is fruitless.

(88) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(89) H. G. Viehe, R. Merényi, J. F. M. Oth, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, 3, 746 (1964).

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# Steric and Polar Rate-Retarding Effects in the Chromic Acid Oxidation of Alcohols

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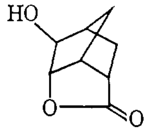
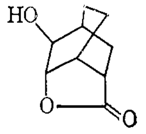
*Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680, and the Department of Chemistry, The Catholic University of America, Washington, D. C. 20017.* *Received May 20, 1967*

**Abstract:** The rates of chromic acid oxidation of a number of cyclic, bicyclic, and bridged bicyclic alcohols have been determined. These are compared with the rates of oxidation for structurally related derivatives bearing electronegative groups. For cyclopentanol, cyclohexanol, 2-*exo*-norbornanol, 2-bicyclo[2.2.2]octanol, 2-*exo*-brendanol, and 6-oxatricyclo[3.2.2.1]decan-4β-ol, relief of steric strain present in the ground state appears to be the dominant factor in controlling the rate of oxidation. Furthermore, for these compounds no correlation exists between the infrared carbonyl stretching frequency of the derived ketone and the rate of chromic acid oxidation of the corresponding secondary alcohol. For the bridged bicyclic and tricyclic lactone alcohol derivatives 5-*exo*,6-*endo*-dihydroxy[2.2.1]heptane-2-*endo*-carboxylic acid lactone (**7**), 5-*exo*,6-*endo*-dihydroxy[2.2.2]octane-2-*endo*-carboxylic acid lactone (**8**), and *trans*-2,3-dihydroxycyclopentaneacetic acid γ-lactone (**9**) very slow rates of oxidation were observed. The large rate retardations are considered to arise from electrostatic destabilization in the transition state between the developing carbonyl group and the polar lactone function.

The chromic acid oxidation of primary and secondary alcohols is well known to be subject to both polar and steric effects. Polar effects generally lead to rate retardations. Thus, the rate of oxidation of a secondary alcohol may be retarded by several orders of magnitude due to the presence within the molecules of strongly electronegative groups.[2,3] Steric effects, on the other hand, may cause impressive rate accelerations.[4] The steric rate acceleration in the chromic acid oxidation of secondary alcohols is believed to be due to the relief of steric strain present in the ground state of the molecule upon its conversion to the ketone. This argument assumes that the transition state for the oxidation resembles the carbonyl product. In agreement with this description, the rate of reaction increases as the number and severity of these ground-state steric interactions are increased. Kwart and Francis[5,6] have challenged this interpretation; they point out that the above mechanistic representation requires a rate retardation in the oxidation of an alcohol leading to a strained ketone. An example which typifies their objection is found in the chromic acid oxidation of 7-norbornanol; its rate of oxidation is only slightly slower than that of 2-*exo*-norbornanol even though the respective carbonyl products differ considerably in degree of internal angular strain at the trigonal carbon atom. At present, no unequivocal example exists of steric retardation in the chromic acid oxidation of a secondary alcohol. What purported to be an example of this phenomenon was a report of the abnormally slow rate of oxidation of certain bridged hydroxy lactones in the bicycloheptane series. Crundwell and Templeton[7] found that hydroxy lactone **7** was highly resistant to oxidation by chromic acid; in fact, they were unable to obtain any of the corresponding keto lactone **12**. Furthermore, this lack of reactivity appeared to be restricted to the bicycloheptane compound since the corresponding [2.2.2]bicyclooctyl hydroxy lactone **8** behaved normally toward chromic acid oxidation. Crundwell and Templeton concluded that the unreactivity of **7** represented an example of steric rate retardation due to the



**7**



**8**

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(1) (a) University of Illinois at Chicago Circle, Chicago, Ill. (b) The Catholic University of America, Washington, D. C.

(2) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, 77, 4907 (1955).

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