# Hindered Rotation in Substituted Benzyl Halides

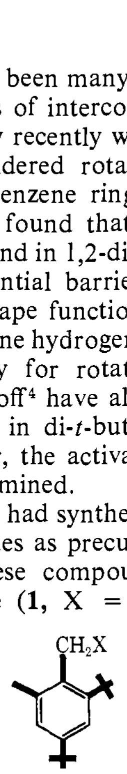
**C. A. Cupas, J. M. Bollinger, and M. Haslanger**[1]

*Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.* *Received April 1, 1968*

**Abstract:** A series of substituted benzyl halides showing hindered internal rotation has been studied using low-temperature nmr techniques. The energy barrier(s) for exchange of the magnetically nonequivalent benzylic hydrogens have been determined for three halides. Evidence is presented that the preferred conformation is that having a benzylic hydrogen eclipsed with the larger *ortho* substituent.

Although there have been many studies by nmr spectroscopy of rates of interconversion between rotational isomers,[2] only recently were there reported the first examples of hindered rotation of alkyl groups attached to a single benzene ring.[3-5] Fraenkel, Newman, and coworkers[3] found that the rate of rotation about the $C_{Ar}$–$CH_2$ bond in 1,2-dineopentyltetramethylbenzene had a substantial barrier to rotation, and by analysis of the line-shape function of the magnetically nonequivalent methylene hydrogens the rate constant(s) and activation energy for rotation was determined. Sternhell and Newsoroff[4] have also presented evidence for hindered rotation in di-*t*-butylphenylcarbinol. In this example, however, the activation energy for rotation has yet to be determined.

In a recent study we had synthesized a variety of substituted benzyl chlorides as precursors to stable benzyl cations.[6] One of these compounds, 2,4-di-*t*-butyl-6-methylbenzyl chloride (**1**, X = Cl), showed a substantial barrier to rotation about the $C_{Ar}$–$CH_2$ bond. In view of the current interest in rotational barriers,[3,4,7,8] we have investigated by the nmr method various derivatives of **1** in order to determine the effects of substituents on the barrier height.



**1**

## Results and Discussion

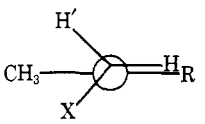
Examination of the low-temperature (−60°) nmr spectrum of **1** (X = Cl) in carbon disulfide showed a typical AB quartet for the benzylic hydrogens where $\delta_{AB}$ = 28.8 Hz and $J_{AB}$ = 11.5 Hz. The exchange rates for the magnetically nonequivalent benzylic hydrogens were determined by comparing the experimental line shapes with those of theoretical spectra having various values of the mean lifetime ($\tau$).[9,10] The exchange rates of the benzylic hydrogens in **1** (X = Br, I) were also measurable in the same manner. In each case, $\tau$ was adjusted until the theoretical spectra were identical with those obtained experimentally. A comparison of the experimental and calculated line shapes for **1** (X = Br) are shown in Figure 1. The pertinent data obtained for this series are summarized in Table I. The low-temperature spectra of **1** (X = F, OH, $OCH_3$) were also examined. However, no broadening of the benzylic hydrogens was observed down to −80°.

**Table I**

| | ($\gamma_A$ − $\gamma_B$),[a] Hz | $J_{AB}$, Hz | $T_c$,[b] °C | $E_a$, kcal | log $A$[c] |
|---|---|---|---|---|---|
| **1**, X = Cl | 28.8 | 11.5 | −30 | 11.3 ± 0.5 | 12.0 ± 0.5 |
| **1**, X = Br | 25.8 | 10.8 | −10 | 12.5 ± 0.5 | 11.8 ± 0.4 |
| **1**, X = I | 24.0 | 9.8 | +19 | 15.9 ± 0.7 | 13.5 ± 0.6 |

[a] All spectra were determined in carbon disulfide. [b] $T_c$, the coalescence temperature, was taken as the temperature at which maximum broadening occurred. [c] Errors are reported as the root-mean-squared error from the least-squares line.

Of the rotamers of **1** to be regarded as energy minima, only conformers **2**, **3**, and **4** (R = *t*-butyl) need be considered since other conformers such as **5**, **6**, or **7** would



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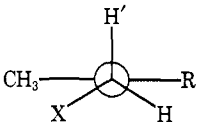

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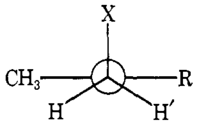

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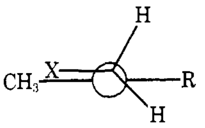

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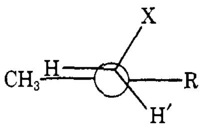

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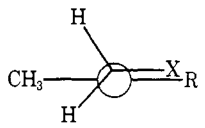

**7**

result in less favorable halogen–alkyl interaction and/or result in magnetic equivalence of the benzylic hydrogens. Since the preferred conformations about $sp^2$–$sp^3$ hybridized carbon atoms have been found to be those where a single bond eclipses the double bond,[7,8,11]

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[1] National Science Foundation Undergraduate Research Participant.

[2] For a review see L. W. Reeves, *Advan. Phys. Org. Chem.*, 3, 187 (1965).

[3] D. T. Dix, G. Fraenkel, H. A. Karnes, and M. S. Newman, *Tetrahedron Letters*, 517 (1966).

[4] G. P. Newsoroff and S. Sternhell, *ibid.*, 2539 (1967).

[5] Hindered rotation of 2-F,6-X-benzotrifluorides and other derivatives have also been reported: J. Jonas, L. Borowski, and H. S. Gutowsky, *J. Chem. Phys.*, 47, 2441 (1967).

[6] J. M. Bollinger, M. Comisarow, C. A. Cupas, and G. A. Olah, *J. Am. Chem. Soc.*, 89, 5687 (1967); C. A. Cupas, G. Olah, and M. Comisarow, *ibid.*, 88, 361 (1966).

[7] For a review see J. Dale, *Tetrahedron*, 22, 3373 (1966).

[8] G. J. Karabatsos and K. L. Krumel, *ibid.*, 23, 1097 (1967), and references therein cited.

[9] The theoretical spectra were calculated by means of a FORTRAN IV coded program based on equations of Alexander: S. Alexander, *J. Chem. Phys.*, 40, 2741 (1964); for these calculations $T_2$ was determined from the width at half-height of a line of the AB quartet under conditions of no exchange; $1/T_2^0$ was assumed to be negligible.

[10] We are indebted to Dr. T. Gerig of the University of California, Santa Barbara, for supplying this program.

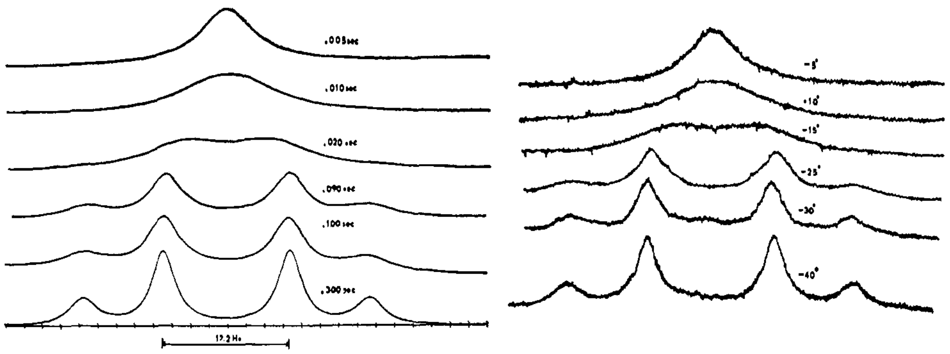

Figure 1. Calculated and experimental spectra of **1** (X = Br) in carbon disulfide.

conformer **2** (where H is eclipsed with the *t*-butyl group) rather than **3** or **4** is the most likely energy minimum.

A further interesting observation which is particularly relevant to the question of **2** as the energy minimum is the trend and magnitude of $J_{AB}$ in the series **1** (X = Cl, Br, I). These values (Table I) are almost identical with those of their corresponding methyl halides. Thus, $J_{AB}$ (Hz) = $\pm 10.8$ ($CH_3Cl$); $\pm 10.2$ ($CH_3Br$); $\pm 9.2$ ($CH_3I$).[12] The similarity in coupling constants is initially surprising since $\pi$-bond effects would be anticipated to effect the magnitude of $J_{AB}$ in **1**. However, as predicted in a theory developed by Barfield and Grant,[13] the effect of adjacent $\pi$ electrons on the geminal coupling constant is dependent on the orientation with respect to the $\pi$ bond. In rotamer **2**, this $\pi$-bond contribution should be negligible since one proton is in the nodal plane of the $\pi$ orbitals.

The potential energy curve for **1** can perhaps best be described as having an asymmetric threefold barrier as depicted in Figure 2. Alternatively, if rotamer **6** is a higher energy minimum, a fivefold barrier would result. Regardless of the exact *n*-fold nature of the barrier, at coalescence temperature, in the nmr experiment, the halomethylene group is not freely rotating. The rotational barrier being measured is simply the exchange process **2** → **2′**, *via* the energy maximum **5**.

Interestingly, the activation energy for rotation increases in the series **1** (X = Cl, Br, I) while the effective size of the halogen groups as determined by their conformational energies in cyclohexane is in the order Cl ≅ I > Br.[14] However, examination of models of rotamer **5** explains this anomaly since a substantial "end-to-end" type van der Waals repulsion of the halogen and methyl hydrogen is present. This latter interaction is absent in axial cyclohexyl halide.

It should be further noted that conformer **2** will be the energy minimum when and only when the flanking *ortho* substituent R is effectively larger than that of the other *ortho* substituent (in this case, $CH_3$). For example, if **2** were to remain as the energy minimum when R = H, a rotational barrier similar to or greater than that found for the series **1** might be anticipated since this substitution would effectively lower the energy of conformer **2** more than that of the energy maximum conformer **5**.

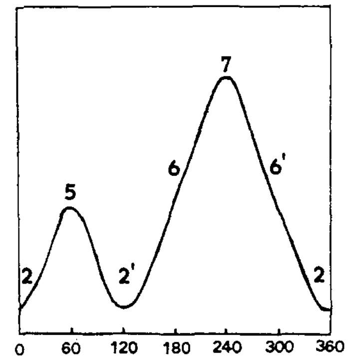

Figure 2. Potential energy diagram of **1** as a function of the rotational angle of the $CH_2$–X group.

In this particular case, then conformer **6** (R = H) would be the energy minimum.

## Experimental Section

The following compounds were prepared according to Beets, Meerburg, and Van Essen:[15] 2-methyl-4,6-di-*t*-butylbenzyl chloride, 2-methyl-4,6-di-*t*-butylbenzyl alcohol, 1-methoxy-2-methyl-4,6-di-*t*-butylbenzene, and 2,5-di-*t*-butylbenzyl chloride.

**2-Methyl-4,6-di-*t*-butylbenzyl Bromide.** 2-Methyl-4,6-di-*t*-butylbenzyl alcohol, 2.0 g (8.5 mmol), was dissolved in 10 ml of methylene chloride and slowly added to phosphorus tribromide which had been cooled in an ice bath. After addition of the methylene chloride solution (10 min) the reaction mixture was stirred at 0° for an additional 15 min and then poured on ice. The aqueous solution was extracted with 100 ml of ether. The ether extract was washed with dilute sodium bicarbonate solution, dried, and distilled. There was obtained 2.1 g, 84%, of a clear viscous liquid, bp 84–86° (0.1 mm). We were unable to induce this material to crystallize.

*Anal.* Calcd for $C_{16}H_{25}Br$: C, 64.64; H, 8.48; Br, 26.88. Found: C, 64.45; H, 8.51; Br, 26.98.

**2-Methyl-4,6-di-*t*-butylbenzyl Iodide.** A solution of 2.5 g (10 mmol) of 2-methyl-4,6-di-*t*-butylbenzyl chloride and 2.3 g (15 mmol) of sodium iodide in 30 ml of dry acetone was refluxed for 2 hr. At the end of this time the brown reaction mixture containing a white precipitate was poured into cold water and the organic material taken up in pentane. The pentane extract was washed once with dilute sodium bisulfite and three times with water and dried. The solvent was removed on a rotary evaporator and used as obtained. This oil was free of extraneous absorptions in its nmr spectrum. The absence of chloride was demonstrated by the

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(11) (a) E. L. Eliel, N. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 19; (b) J. Jonas, L. Borowski, and H. S. Gutowsky, *J. Chem. Phys.*, 47, 2441 (1967); (c) K. Radcliffe, and J. L. Wood, *Trans. Faraday Soc.*, 62, 2038 (1966).

(12) For a review see A. A. Bothner-By, *Advan. Magnetic Resonance*, 1, 195 (1965).

(13) (a) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, 45, 1899 (1963); (b) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, 1, 149 (1965).

(14) See J. A. Hirsch in "Topics in Stereo-Chemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 199.

(15) M. G. J. Beets, W. Meerburg, and H. Van Essen, *Rec. Trav. Chem.*, 78, 570 (1959).

disappearance of the 675-cm$^{-1}$ band present in the starting material. The presence of iodine in the product was demonstrated by the appearance of a violet color in samples allowed to stand at room temperature and by treating a sample of the material with alcoholic silver nitrate.

**2-Methyl-4,6-di-*t*-butylbenzyl Fluoride.** To a solution of 10.1 g (40 mmol) of 2-methyl-4,6-di-*t*-butylbenzyl chloride in 50 ml of anhydrous acetonitrile was added 12.7 g (100 mmol) of anhydrous silver (argentous) fluoride (Harshaw). The resulting mixture was stirred without heating for 4 hr, filtered, and poured into cold water. The organic layer was taken up in pentane, washed five times with cold water, dried, and distilled. There was obtained 5.6 g of the desired product, bp 90–94° (3 mm) (methylene doublet at $\delta$ 5.85 ppm, $J_{HF} = 49$ Hz in carbon disulfide relative to TMS internal).

*Anal.* Calcd for $C_{16}H_{25}F$: C, 81.30; H, 10.66; F, 8.04. Found: C, 81.37; H, 10.60; F, 8.33.

**Nmr Measurements.** Nmr spectra were measured on a Varian A56-60A spectrometer equipped with a variable-temperature probe. Temperature measurements were accomplished with a thermometer which fitted an nmr tube and which was calibrated at 0° (ice water) and −78° (Dry Ice in acetone) and checked against the chemical shift difference of the methanol signals.

Spectra were obtained on approximately 25 (v/v) solutions in carbon disulfide. Measurement of the coalescence temperatures in chloroform gave the same results within experimental error.

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# Base-Catalyzed Deuterium Exchange of Acyclic Sulfones

**C. D. Broaddus**

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**Abstract:** A series of alkyl and alkenyl methyl sulfones was subjected to deuterioxide-catalyzed exchange in deuterium oxide–dioxane solvent at 25°. The results are summarized in Table I. It was shown that 2-hydroxyhexyl methyl sulfone was stable to these exchange conditions. From these results the following conclusions may be drawn. (1) Increased alkyl substitution at a carbon adjacent to a sulfone substituent strongly retards the rate of carbanion formation relative to similar substitution changes in nitroalkanes and ketones. (2) The rate of exchange of an $-SO_2CH_3$ site is little affected by the other hydrocarbon group attached to a sulfone substituent whether it be alkyl, 1-alkenyl, or 2-alkenyl. (3) Alkyl-substituted allyl anionic species generated adjacent to a sulfone group undergo very specific protonation at the site next to the sulfone group. The difference in activation energies for the two protonation reactions is larger than the difference in ground-state energies of 1- and 2-alkenyl methyl sulfones. (4) Replacement of hydrogen on a carbon adjacent to a sulfone group by a 1-pentenyl substituent increases the rate of base-catalyzed deuterium exchange by a factor of ~10. Replacement of *n*-propyl by 1-pentenyl causes a ~10$^4$ increase in rate of exchange. (5) 1-Alkenyl methyl sulfones undergo most rapid exchange at the $\alpha$-methyl position. The $\alpha$-vinyl hydrogen is exchanged, by a proton abstraction mechanism, somewhat more rapidly than reaction occurs at the allylic site. (6) Little difference is seen in the reactivities of *cis*- and *trans*-1-alkenyl methyl sulfones or in the reactivities of *cis*- and *trans*-2-alkenyl methyl sulfones.

The subject of carbanionic intermediates adjacent to an activating sulfone substituent has received extensive study.[1] In some recent work it was observed[2] that base-catalyzed deuterium exchange of 2,3-dihydrothiophene 1,1-dioxide resulted in rapid vinyl as compared to allyl proton abstraction. Anionic reactions in unsaturated cyclic sulfones could be influenced by such factors as hybridization changes due to inclusion in a small ring, configurational preferences of the carbanionic species, and ring-strain effects. Therefore, it was felt that a study of acyclic systems should be performed to minimize the number of variables. Since there is little background information in this particular area, the relative reactivities at various positions of saturated, $\alpha,\beta$-unsaturated, and $\beta,\gamma$-unsaturated acyclic sulfones have been determined. As described in the Results only three points were taken in each kinetic run and the extent of deuteration was determined from proton magnetic resonance spectra. While this work does not provide precise kinetic data, the observed reactivities allow considerable insight into carbanionic reactions of sulfones.

## Results

The results of these base-catalyzed exchange studies are summarized in Table I. The extent and positions of deuterium exchange were determined by removing at least three portions at timed intervals from basic solutions placed in a thermostated bath at 25.0°. The data necessary for construction of Table I were obtained by integration of proton magnetic resonance (pmr) spectra using the terminal methyl of the alkyl chain as an internal standard. Examples of typical runs are presented in Table III of the Experimental Section. First-order rate constants were obtained by plotting the logarithim of the change in relative area of the position undergoing exchange against time. The best straight line was selected visually. Several "one-point" determinations were performed to establish that the concentration of base remained constant during these exchange processes (see Experimental Section). The much more complete kinetic analysis of base-catalyzed deuterium exchange of dimethyl sulfone[3]

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(1) (a) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84; (b) D. J. Cram, R. D. Trepka, and P. St. Janiak, *J. Amer. Chem. Soc.*, **88**, 2749 (1966); (c) S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.*, *B*, 348 (1967); H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, *ibid.*, 4101 (1964), for leading references.

(2) C. D. Broaddus, *J. Amer. Chem. Soc.*, **88**, 3863 (1966).

(3) J. Hochberg and K. F. Bonhoeffer, *Z. Phys. Chem.*, **A184**, 419 (1939).