purchased from Miles Laboratories, Inc., Elkhart, Ind. 46514. Solute concentrations in the cholesteric mesophases were normally between 10^{-2} and 10^{-3} *M*.

In summary, LCICD of noncomplexing achiral molecules has been observed in lyotropic cholesteric mesophases composed of PBLG and PBDG in a variety of helix supporting solvents. LCICD of anthracene in lyotropic cholesteric mesophases is distinctly different from that found in thermotropic cholesteric mesophases which is tentatively attributed to a variation in the ability of the two cholesteric mesophase types to order anthracene single molecules or possibly the intervention of the previously suggested mechanism b.

Acknowledgment. Stimulating discussions with Drs. W. H. H. Gunther, G. Johnson, H. Gibson, and J. E. Kuder are gratefully acknowledged.

(20) Rochester Institute of Technology Co-op.

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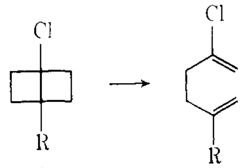
Ring Opening of Bicyclo[2.2.0]hexanes. Effect of Alkyl Group Substitution upon Interpretation of Radical Stabilization Energies

Sir:

Without exception, the substitution of an alkyl group for a hydrogen atom in a series of aliphatic hydrocarbons will decrease the α-bond strength.[1] This decrease is made up of a contribution from increased steric (gauche) interactions in the parent molecule and an increased stability of the radical formed in the series tertiary > secondary > primary.[2] The picture is not so clear for cyclic hydrocarbons, as in several cases alkyl substitution increases the activation energy for α-bond scission.[2] Within the approximations of the biradical mechanism, O'Neal and Benson[2] have shown that radical stabilization energies derived from cyclic compounds are in reasonable agreement with those derived from acyclic compounds.[3] To explain a large increase found in the activation energy for the ring opening of 1,1,3,3-tetramethylcyclobutane, Cocks and Frey[4] introduced a further variable into the mechanism, that of steric interactions in the ring opening of cyclobutanes. Our studies on the bicyclo[2.2.0]hexane system have now reached a stage where we can conclude that our results are not in agreement with the above postulates. These results are presented in their present form due to the possible effect on the large volume of work which incorporates the above assumptions.

1-Chloro-4-methylbicyclo[2.2.0]hexane (**1**, R = CH_3) was prepared from 1-chloro-4-hydroxymethylbicyclo-[2.2.0]hexane[5] (**1**, R = CH_2OH) by hydride displacement of the mesylate (**1**, R = CH_2OMs; recrystallized from hexane; mp 47°) with $LiAlH_4$. 1-Chloro-4-ethylbicyclo[2.2.0]hexane (**1**, R = CH_2CH_3) was obtained by photochemical (Hanovia 450 W, Pyrex filter, MeOH) Arndt–Eistert homolygation of the acid[5] (**1**, R = CO_2H) followed by $LiAlH_4$ reduction of the ester (**1**, R = $CH_2CO_2CH_3$) to the alcohol (**1**, R = CH_2CH_2OH), mesylate (mp 55°) formation, and hydride displacement with $LiAlH_4$.



1 2

The rate of ring opening of these two alkyl derivatives (**1**, R = CH_3 and C_2H_5) to the dienes (**2**, R = CH_3 and C_2H_5) was measured both in the gas phase and in solution (over the temperature range 136.5–238.6°) as previously described.[6,7] Least-squares calculations on the results gave the following Arrhenius equations for the 4-methyl derivative: $\log (k_g/\text{sec}^{-1}) = (13.86 \pm 0.03) - (36.90 \pm 0.07)/\theta$; $\log (k_a/\text{sec}^{-1}) = (13.55 \pm 0.31) - (35.50 \pm 0.13)/\theta$; $\log (k_b/\text{sec}^{-1}) = (13.64 \pm 0.30) - (35.68 \pm 0.13)/\theta$. The following equations were derived for the 4-ethyl derivative: $\log (k_a/\text{sec}^{-1}) = (13.68 \pm 0.29) - (36.19 \pm 0.13)/\theta$ and $\log (k_b/\text{sec}^{-1}) = (13.55 \pm 0.15) - (35.87 \pm 0.06)/\theta$, where $\theta = 2.303RT$ kcal/mol, error limits are least-squares deviations, and the subscripts g, a, and b refer to the gas phase, tetrachloroethylene, and *o*-dichlorobenzene as solvent, respectively. These may be compared to activation energies for 1-chlorobicyclo[2.2.0]hexane (**1**, R = H) of 35.42, 34.50, and 34.60 kcal/mol and Arrhenius log *A* values of 13.49, 13.21, and 13.25 in the gas phase, tetrachloroethylene, and *o*-dichlorobenzene as solvent, respectively.[8]

Both gas and liquid phase results are consistent with a small but significant increase of 1.2 ± 0.5 kcal/mol in the activation energy when the bridgehead hydrogen atom is replaced by a methyl group; there is an additional small increase in the activation energy on substituting an ethyl group for the bridgehead hydrogen atom.

We have previously obtained excellent group additivity in the following 1,4-disubstituted bicyclo[2.2.0]-hexane series: H,H, H,Cl, Cl,Cl, and Cl,H, Cl,CO_2CH_3, CO_2CH_3,CO_2CH_3—this assumed no 1,4 interactions in the transition complex.[9] From the absence of any interactions between the pairs Cl,CO_2CH_3 and CO_2CH_3,CO_2CH_3 it may be concluded that likewise there will be no 1,4 interaction between the smaller Cl,CH_3 and Cl,C_2H_5 groups. The increase in activation energy on alkyl substitution must be an intrinsic property of the alkyl group and not a result of steric interaction.[10]

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(7) The methyl signal(s) provided a convenient in-built internal standard for checking calculations.

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(10) Srinivasan[11] has previously reported Arrhenius parameters of $\log k(\text{sec}^{-1}) = 11.3 - 31.0/\theta$ for the gas-phase thermal ring opening of 1,4-dimethylbicyclo[2.2.0]hexane. These results are not consistent with our conclusion. However, Srinivasan's kinetics indicate a large negative entropy of activation and on the basis of a concerted or biradical mechanism, such a value is not possible from transition state theory for the ring opening of such a rigid molecule. It is interesting to note that if we put the Arrhenius *A* factor in the "more normal" range of $10^{14.0\pm0.5}$ sec^{-1} an approximate activation energy of 37.0 kcal/mol is obtained—this is then in excellent agreement with our conclusion (*vide supra*) of an intrinsic increase in activation energy of 1.2 ± 0.5 kcal/mol per methyl group.

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Application of this conclusion depends upon the mechanism[12] for the ring opening of bicyclo[2.2.0]-hexanes. If it is biradical, and our preferences are in this direction for the reasons discussed in our most recent paper,[9] then either the general applicability of radical stabilization energies or the commonly accepted alkyl group stabilization must be questioned. If the isomerization occurs *via* a concerted process, there is no doubt that there is an intrinsic increase in activation energy with alkyl substitution in the bicyclo[2.2.0]-hexane series and that this can likely be extrapolated to analogous cyclic compound isomerizations.

Acknowledgments. A Queen Elizabeth II Fellowship and the hospitality of the University of New South Wales to R. K. S. are gratefully acknowledged.

[12] A detailed mechanistic discussion will be presented in a forthcoming publication. We believe the mechanism involves a radical-like intermediate which opens stereoselectively as proposed by Paquette.[13] *Cf.* recent papers by Goldstein[14] and van Rantwijk.[15]

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Steric Hindrance in Molecular Beam Reactions

Sir:

Intuitive considerations of molecular geometry have for many years provided considerable insight into the rate and mechanism of many chemical reactions,[1] and on a routine basis one invokes the qualitative notion that "bulky groups" can shield "reactive sites" or can interfere with the formation of a transition state. These notions regarding steric hindrance are sufficiently appealing and useful to warrant study by as direct means as possible. Crossed molecular beam techniques are ideally suited to this purpose since the reaction of isolated molecules (which can easily be state selected or oriented) can be studied, and indeed the direct observation of a steric effect was reported some time ago.[2] Subsequent work has been mainly concerned with development of techniques[3] and kinematic details.[4] In this communication we wish to report on the reactivity of several oriented molecules which exhibit a wide range of behavior which is not always predicted by chemical intuition.

The experimental concept is unchanged from the early experiments[2] and is discussed in detail in ref 3. Briefly, a beam of molecules is passed through a combination of electric fields which can *select* molecules in a range of orientation which can correspond to the reactive end pointing either *toward* the incoming reactive atom ("heads"), or *away* from the incoming atom ("tails"). The orientation may be reversed by changing the polarity of a weak electric field.[5] The experimental observations are the product angular distributions resulting from either the "heads" or "tails" distributions.

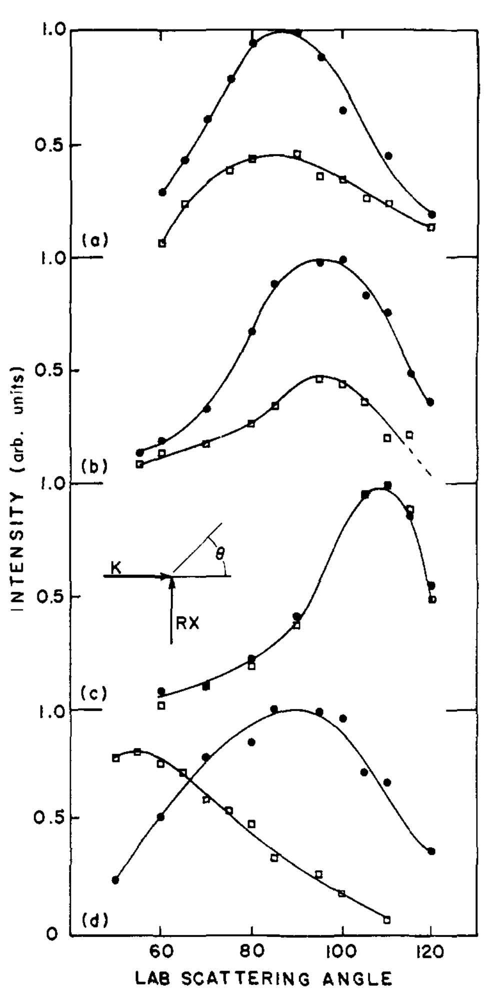

Figure 1. Laboratory angular distributions of reactively scattered KI (or KCl) for (a) CH_3I, (b) *t*-BuI, (c) $CHCl_3$, (d) CF_3I. Filled points denote reaction from the "heads" configuration in which the reactive end of the molecule points toward the incoming K atom; unfilled points denote reaction from the "tails" configuration. The results for different molecules have been normalized to have the same peak height. In all cases we observe the reactivity of unoriented molecules to be intermediate between the extremes shown.

Potassium atoms have been treated with CH_3I, *t*-BuI, CF_3I, and CCl_3H molecules to form KI or KCl. Typical results are shown in Figure 1. It is apparent that in general a significant difference in reactivity obtains for impact at different ends of the molecules. Furthermore, the existence of such a difference shows that these molecules do not turn to present their most favorable end prior to reaction.

The relative reactivities (the area under the curves) of the "heads" and "tails" configurations for methyl

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[4] (a) R. J. Beuhler, Jr., and R. B. Bernstein, *Chem. Phys. Lett.*, **2**, 166 (1968); (b) P. R. Brooks, *J. Chem. Phys.*, **50**, 5031 (1969; (c) R. J. Beuhler, Jr., and R. B. Bernstein, *ibid.*, **51**, 5305 (1969).

[5] If θ is the average angle between the molecular dipole moment and the relative velocity of the two particles, the "heads" orientation consists of a distribution with $0 < \theta < \pi/2$ and the "tails" orientation with $\pi/2 < \theta < \pi$. In view of the effect on reactivity, the average orientation is surprisingly close to broadside, $\bar{\theta} \simeq 70°$ (or 110°).