

Table I. Relative Reactivities of Alkenes toward Phenylbromocarbene, 25°^a

Case	TME ^b /olefin _i	(a) (k_{TME}/k_i) _{Base} ^c	(b) (k_{TME}/k_i) _{hv} ^d	(c) (k_{TME}/k_i) _{erown} ^e
1	TME-trimethylethylene	1.28 ± 0.09 ₃	1.74 ± 0.04 ₂	1.72 ^f
2	TME-isobutene	1.65 ± 0.217 ^g	4.44 ± 0.18 ₂	4.11 ± 0.14 ₂
3	TME- <i>cis</i> -butene	5.79 ± 0.11 ₂	8.34 ± 0.04 ₂	8.24 ^f
4	TME- <i>trans</i> -butene	11.3 ± 1.6 ₄	17.5 ± 0.8 ₂	17.1 ± 0.4 ₂
5 ^h	TME-isobutene	2.6 ± 0.1 ₃	5.0 ± 0.3 ₆	4.8 ^f

^a Relative reactivities were calculated in the standard⁴ manner,⁵⁻⁷ and mean values are reported. Errors are average deviations from the means of *n* (subscript) experiments. The analytical methods (quantitative nmr) are fully described in ref 5 and 7. ^b TME = tetramethylethylene. ^c 2a + KO-*t*-Bu. ^d 3a + hv. ^e 2a + KO-*t*-Bu + 18-crown-6, this work. ^f Single experiment. The nmr integrals were precise to <4%. ^g 1.83, this work. ^h Phenylchlorocarbene was used; Cl replaces Br throughout.

selectivities of **1a** and **1b**, generated from **2a** and **2b** with KO-*t*-Bu-18-crown-6.¹⁵ The dramatic results confirm our earlier analyses.^{6,7} More importantly, they have major implications for the study of carbenes.

The data in columns b and c of Table I (cases 1-4) show that the olefin selectivity of phenylbromocarbene (**1a**) generated by the addition of **2a** to homogeneous olefin-benzene solutions of 1:1 KO-*t*-Bu/18-crown-6 is experimentally identical with that of **1a** generated by the photolysis of phenylbromodiazirine. Case 5 reveals that a similar identity holds for the only example in which light- and base-generated **1b** had previously led to substantial selectivity differences.

By way of contrast, CCl₂ was generated from CHCl₃ and KO-*t*-Bu in the presence and absence of 18-crown-6 and caused to select between methylenecyclohexane and cyclohexene at 25°. The relative olefin reactivities were 4.79 and 5.51 ± 0.02₂, respectively.¹⁸ Dichlorocarbene is generally believed to be free, even when generated from CHCl₃-KO-*t*-Bu.²⁰ The small variation between crown and noncrown experiments may reflect a solvent effect but is certainly unlike the large changes induced by 18-crown-6 in the selectivities of **1a** and **1b** (Table I, columns a and c).

We conclude the following. (1) Photolysis of **3** generates free phenylhalocarbenes, **1**, eq 1, path C. (2) The same intermediates can be produced from **2** with KO-*t*-Bu-18-crown-6, eq 1, path B. (3) The light-generated species is not a vibrationally excited carbene nor is it a photoexcited diazine or diazo compound; the selectivities of these alternative intermediates should differ from those of the base/crown-generated carbenes. (4) α-Elimination from **2** in the absence of 18-crown-6 leads to phenylhalocarbenoids, which are probably complexes of **1** with either KX or KO-*t*-Bu, eq 1, path A. (5) It should be possible to determine whether certain base-induced α-eliminations afford carbenes or carbenoids by measuring the olefin selectivity of the carbenic species in the presence and absence of crown ether. This test will have wide applicability.⁴ (6) KOR-18-crown-6 α-eliminations should make free carbenes available when diazoalkane or diazine precursors are not readily obtainable.

(15) 1,4,7,10,13,16-Hexaoxacyclooctadecane. The macrocyclic polyether was prepared by the methods of ref 11 or 16 and purified via its acetonitrile complex.¹⁷

(16) C. L. Liotta, H. P. Harris, F. Cook, D. J. Cram, and G. Gokel, *J. Org. Chem.*, in press.¹⁷

(17) Private communication from Professor C. L. Liotta, Georgia Institute of Technology.

(18) $k_{\text{methylenecyclohexane}}/k_{\text{cyclohexene}}$ is 4.57 for CCl₂ derived from C₆H₅CCl₂Br (benzene, ~80°).¹⁹

(19) R. A. Moss and C. B. Mallon, *Tetrahedron Lett.*, 4481 (1973).

(20) Reference 4, pp 287-288, and citations therein.

This should have important consequences for the study of carbene reactivity.⁴

Acknowledgments. We thank the National Science Foundation (GP-32159X) and the National Institutes of Health (CA-14912) for financial support and Professor C. L. Liotta for preprints of the 18-crown-6 synthesis and purification.

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Received July 6, 1974

Indan Anion Radical. An Unambiguous Exemplification of Strong 1,3 p-σ Overlap (Homohyperconjugation) in a Nonrigid System

Sir:

Quantum mechanics informs us unequivocally that orbital overlap between "nonbonded" atoms joined to a common atom (1,3 overlap) is significant. Clear manifestations of such overlap in species other than carbonium ions are still rare, however. This is especially true of the homohyperconjugative (p,σ) as distinguished from the homoconjugative (p,p) variety. We wish to report esr results and INDO-MO calculations on the indan anion radical which establish it as a valid and vivid example of this interesting interaction type.

The esr spectrum of 1⁻ (K⁺, DME, -60°) is given in Figure 1. The hfs are $a_{1,1} = 6.65$ (2 H), $a_{2,3} = 2.20$ (2 H), $a_{\beta} = 4.65$ (4 H), $a_{\lambda} = 1.10$ (2 H), and $a_K = 0.20$ G (quartet); note the pronounced line width alternation. The hyperfine lines are all sufficiently narrow to permit resolution of the small quartet except those of the γ protons, each of which is markedly broadened. Modulation of the λ hfs between its axial and equatorial values ($\Delta a_{\lambda} = a_e - a_{ax}$) at a rate comparable to the frequency difference is occurring and blurring the λ hyperfine lines. The β lines are not similarly broadened, though β proton interconversion must occur at the same rate as for the λ protons. Thus, $\Delta a_{\beta} < \Delta a_{\lambda}$. That this is so even though \bar{a}_{β} is much larger than \bar{a}_{λ} and itself critically ($\cos^2 \theta$) conformation dependent is startling and novel. 1,3-Interactions provide a unique, simple explanation for this singular behavior by dramatically decreasing Δa_{β} while increasing Δa_{λ} .

INDO-MO calculations for the indan and cyclopentene anion radicals were carried out keeping $\theta_{ax} = 1.2^\circ$ and $\theta_{eq} = 58.8^\circ$ for the β protons, where θ

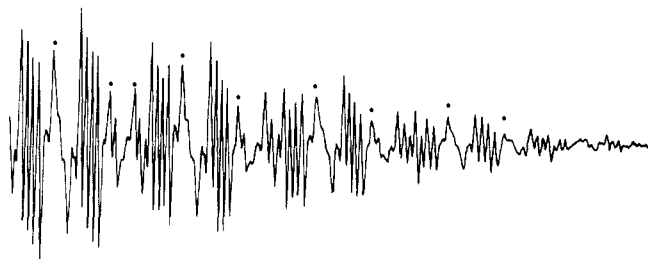
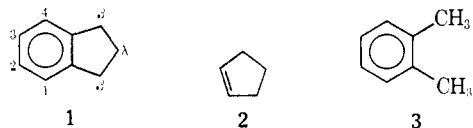


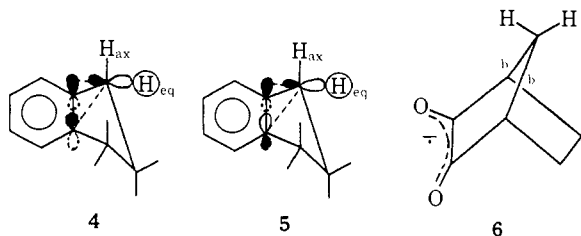
Figure 1. Indan anion radical (K^+ , DMF, -60°). Half spectrum shown. The starred absorption envelopes represent the γ hfs lines.

is the usual dihedral angle.¹ The $\cos^2 \theta$ law thus predicts $a_{ax}^\beta/a_{eq}^\beta = 3.72$. For $2\cdot^-$ the INDO calculated ratio is 4.34. The $1\cdot^-$ calculation, using benzene parameters for the aromatic moiety, gives 3.91. This anion radical, which we will call $a\text{-}1\cdot^-$, is not the experimental species, however; the odd electron in it occupies an antisymmetric benzene-like ABMO, that in the observed species occupies a symmetrical ABMO. To simulate $s\text{-}1\cdot^-$, the bridge and 2,3 C-C bonds were shortened (1.340 Å), as they should actually be in this species. The calculated hfs now agree well with experiment ($a_{1,7} = -8.78$, $a_{5,6} = -1.16$, $\bar{a}_\beta = 4.16$, $\bar{a}_\lambda = 0.47$). The $a_{ax}^\beta/a_{eq}^\beta$ ratio is now 1.66, far lower than predicted by $\cos^2 \theta$ and than calculated for the two antisymmetric species ($a\text{-}1\cdot^-$ and $2\cdot^-$). The latter, in contradistinction, have ratios greater than the $\cos^2 \theta$ prediction. Further, the λ hfs also exhibit the required dependence on symmetry: for $s\text{-}1\cdot^-$, $\Delta a = 1.22$; for $a\text{-}1\cdot^-$, $\Delta a = 0.44$; for $2\cdot^-$, $\Delta a = 0.50$. Finally, \bar{a} (both calculated and observed) is abnormally large for $s\text{-}1\cdot^-$ in comparison to the acyclic, *o*-xylene case. The β (*i.e.*, methyl) hfs in $3\cdot^-$ is only 2.0 G; adjusting for the different



($\cos^2 \theta$) in $3\cdot^-$ and $s\text{-}1\cdot^-$ raises this to 2.53 G. Consideration of spin density differences merely heightens the contrast. Therefore in the s species, specifically, $a_{ax}^\beta/a_{eq}^\beta$ are being selectively and greatly enlarged and, conversely, are attenuated in the two a species.

Homohyperconjugation explains these observations fully, fluently, and uniquely. Structures 4 and 5 illustrate the overlap in $s\text{-}1\cdot^-$ and $a\text{-}1\cdot^-$, respectively. One notes simply that hyperconjugative (1,2) and homohyperconjugative (1,3) overlap reinforce in 4 and interfere in 5. The same applies for the γ -protons. That the effect is greater with an equatorial than an axial bond reflects more efficient $\sigma\text{-}\pi$ overlap with the back lobe of an equatorial sp^3 orbital than overlap with an axial orbital. Semidione, 6, is an important



(1) Bond lengths and angles were adopted from M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74**, 1104 (1970).

precedent for stereospecificity in long range interactions.² The effect has also previously been seen in nonrigid systems and equatorial selectivity demonstrated.^{3,4} However, $s\text{-}1\cdot^-$ constitutes a more unambiguous example of direct (through space) 1,3 overlap. In previous examples, such as $6\cdot^-$, bonds b are nonorthogonal to the π system and potentially provide an *indirect* (through bond) route to long range coupling.

An estimate of the magnitude of the energy perturbation in $s\text{-}1\cdot^-$ is not available, but whatever its magnitude, it is clear that at least three relatively strong 1,3 overlaps are present in the molecule and exert amazingly large effects on its spin and charge density distributions. Finally, the important effect of these findings upon esr based conformational analysis should not be overlooked.

Acknowledgment. The authors are grateful to the Robert A. Welch Foundation (F-149) for generous support of this research.

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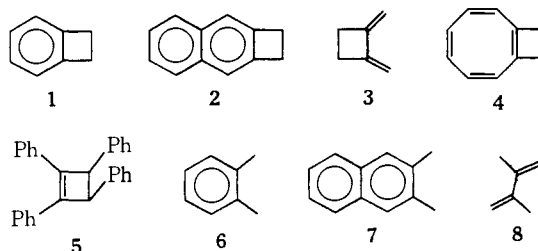
Received April 19, 1974

Quantitative Aspects of 1,3 $p\text{-}\sigma$ Overlap across a Cyclobutane Ring in Anion Radicals

Sir:

1,3-Interactions in the indan anion radical engender quite dramatic effects on its spin and charge density distributions.¹ Cyclobutane rings, having shorter 1,3 C-C distances, should sustain 1,3-interactions of even greater magnitude. Esr data on the series of cyclobutenoid radicals 1-5 \cdot^- confirm this expectation and permit the first quantitative experimental evaluation of the efficiency of 1,3 $p\text{-}\sigma$ overlap relative to 1,2 overlap.

Recent results have revealed abnormally large esr hfs for 1-3 \cdot^- .² Although cyclobutene methylenes, on the basis of their dihedral angle, should have hfs *ca.* 60% greater than freely rotating (*e.g.*, methyl) protons, the values of a_{CH_2} for 1 \cdot^- , 2 \cdot^- , and 3 \cdot^- exceed a_{CH_2} of the *o*-xylene (6 \cdot^-), 2,3-dimethylnaphthalene (7 \cdot^-), and 2,3-dimethyl-1,3-butadiene (8 \cdot^-) anion radicals by 165,



244, and 538%, respectively. Since the spin densities at, *e.g.*, positions 2-5 of 1 \cdot^- are not decreased at all relative

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