

Figure 1. A 220-MHz pmr spectrum of the N-H resonances of 0.5 M $\text{PhC}(\text{NH}_2)_2^+$ in aqueous H_2SO_4 at 20°.

effects that increase the stability of **7** are responsible for the 6.4-fold rate difference.

Unsubstituted amidinium ions provide unambiguous proof. In 20% aqueous H_2SO_4 , benzamidinium ion (**1**, R = Ph) shows two broad (width 12 Hz) N-H resonances downfield of the phenyl and solvent resonances. By analogy to amides,⁸ the low-field resonance may be attributed to H_E . With increasing H_2SO_4 content, these peaks shift upfield without broadening, and the low-field peak shifts more rapidly. From 30 to 65% H_2SO_4 the N-H peaks are obscured under phenyl or solvent resonances. In 70% H_2SO_4 the two peaks are again observable. The one at higher field is slightly broader (Figure 1). With increasing H_2SO_4 content both peaks undergo further broadening, with the one at higher field always distinctly broader (Figure 1).

This observation demonstrates that the diastereotopic hydrogens of benzamidinium ion undergo acid-catalyzed exchange at different rates and that the hydrogens of the $-\text{NH}_3^+$ group do not become equivalent. From the extent of the broadening, the rate ratio is calculated to be 3:1, corresponding to a barrier height of ~ 3 kcal/mol. We cannot be certain that H_E is the faster to exchange, as the above argument suggests, but this is consistent with the behavior of the chemical shifts and also with the exchange rates in the N,N' -dimethyl analog.^{2b} We therefore conclude that there is a chemically significant barrier to rotation about the C-N single bond of $\text{RC}(\text{NH}_3^+) = \text{NH}_2^+$, which is produced in a conformation (**3**) that requires that the "outside" hydrogen exchange faster than the "inside" one. We have thus demonstrated a novel conformational effect that is, to our knowledge, entirely without precedent.

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(8) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970).

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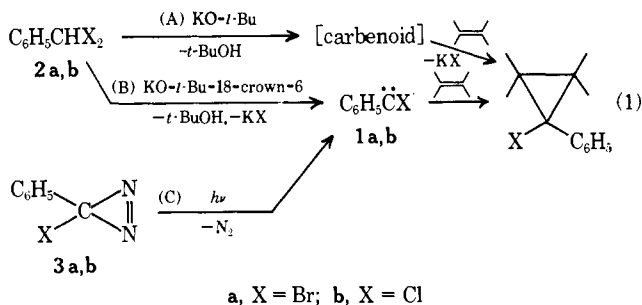
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Crown Ethers in Carbene Chemistry. The Generation of Free Phenylhalocarbenes

Sir:

A basic uncertainty accompanying carbene generation by base-induced α -elimination has heretofore been the "freeness" of the carbenic species. With haloorganic progenitors, carbenoids were often encountered.¹ Our interest in carbenic reactivity⁴ led us to determine the selectivity toward alkenes of phenylbromocarbene (**1a**)^{5,6} and phenylchlorocarbene (**1b**),⁷ generated either by treatment of the requisite benzal halides (**2**) with potassium *tert*-butoxide^{5,7} or by photolysis of the corresponding phenylhalodiazirines (**3**)^{6,7}; see eq 1,



paths A and C, respectively.

The selectivities of the base- and light-generated "carbenes" were clearly different, as is shown in Table I (columns a and b). A conventional explanation was offered. The photolytic intermediate was a free carbene, whereas the base-generated intermediate was a carbenoid—either a phenylhalocarbene-potassium halide complex or a phenylhalocarbene-potassium *tert*-butoxide⁸ complex. If this explanation is correct, then it should be possible to generate free phenylhalocarbenes by the base-induced α -elimination reaction, provided that the potassium cation or the solid $\text{KO-}t\text{-Bu}$ can be rendered unavailable for complexation with the carbene.

Crown ethers¹⁰ complex various cations, and K^+ is particularly well complexed by the 18-crown-6 ethers.^{10,11} In their presence, KMnO_4 ¹² and KF ¹³ become useful reagents in organic solvents; $\text{KO-}t\text{-Bu}$ can be solubilized, and its dissociation and reactivity are enhanced.¹⁴ We therefore examined the olefin

(1) The noun "carbenoid" defines an intermediate "which exhibit(s) reactions qualitatively similar to those of carbenes without necessarily being (a) free divalent carbon species."^{2,3}

(2) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

(3) See W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 5 ff.

(4) R. A. Moss in "Carbenes," Vol. 1, M. Jones, Jr., and R. A. Moss, Ed, Wiley, New York, N. Y., 1973, p 153 ff.

(5) R. A. Moss and R. Gerstl, *Tetrahedron*, **22**, 2637 (1966).

(6) R. A. Moss, *Tetrahedron Lett.*, 4905 (1967).

(7) R. A. Moss, J. R. Whittle, and P. Freidenreich, *J. Org. Chem.*, **34**, 2220 (1969).

(8) Potassium *tert*-butoxide is associated in nonpolar solvents.⁹ Moreover, the benzal halide-potassium *tert*-butoxide-alkene reaction mixtures were heterogeneous.⁵

(9) D. E. Pearson and C. A. Buehler, *Chem. Rev.*, **74**, 45 (1974).

(10) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386 391 (1970).

(11) R. N. Greene, *Tetrahedron Lett.*, 1793 (1972).

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(13) C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.*, **96**, 2250 (1974).

(14) J. N. Roitman and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2231 (1971); M. J. Maskornick, *Tetrahedron Lett.*, 1797 (1972); R. A. Bartsch, G. M. Pruss, R. L. Buswell, and R. A. Bushaw, *ibid.*, 2621 (1972); R. A. Bartsch and K. E. Wieggers, *ibid.*, 3819 (1972).

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) _{crowne} ^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

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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 $a_{1,4} = 6.65$ (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