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CARBENES AND CARBENOIDS -- CROWN ETHER AND CARBENIC SELECTIVITY EXPERIMENTS WITH PHENYLFLUOROCARBENE AND CHLOROMETHYLTHIOCARBENE

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Phenylchlorocarbene and phenylbromocarbene could be generated as free carbenes by the action of KO-t-Bu on α,α-dihalotoluenes, if the macrocyclic polyether, 18-crown-6, was used to encapsulate the potassium ion, solubilize the base, and bar them from complexation with the carbenes (carbenoid formation).[2] Importantly, this work implied that "it should be possible to determine whether (other) base-induced α-eliminations afford carbenes or carbenoids by measuring the olefin selectivity in the presence and absence of crown ether...," and that "KOR-18-crown-6 α-eliminations should make free carbenes available when diazoalkane or diazirine precursors are not readily obtainable."[2] We report here on the successful implementation of these ideas, and on important consequences for the study of carbenic selectivity.[3]

Phenylfluorocarbene[4] and chloromethylthiocarbene[5] were generated from α-bromo-α-fluorotoluene and α,α-dichlorodimethylsulfide, respectively, by the action of potassium t-butoxide, with or without an added equivalent of 18-crown-6.[6] These species were added to tetramethylethylene, trimethylethylene, isobutene, cis-butene, and trans-butene. Except for the adduct of CH_3SCCl and cis-butene,[7] full characterizations of the cyclopropane products have been published.[4,5]

Carbenic selectivities were established at 25° using the olefin competition method,[8] in which the binary cyclopropane product mixtures resulting from pairs of competing olefins were analyzed by gc[9] (calibrated TC detector). Relative reactivities of the olefins were calculated in the standard manner.[8] Average deviations from the means of duplicate experiments were <4%, and satisfactory cross-checks[8] were obtained. Final relative reactivities, normalized to $k_{isobutene} = 1.00$, appear in Table I, along with analogous data for related carbenic species. Also included are values of m_{CXY}^{obsd}, the least-squares slope of log $(k_i/k_{isobutene})$ for CXY vs.

log ($k_i/k_{isobutene}$) for CCl_2, at 25°. We have shown that m_{CXY}^{obsd} of (free) CH_3CCl, C_6H_5CBr, C_6H_5CCl, CCl_2, CFCl, and CF_2 are correlated by eq. (1).[3] m_{CXY} is a measure of carbenic selectivity, relative to the selectivity of CCl_2 (m = 1.0).[3]

$$m_{CXY} = -0.94\sum_{X,Y}\sigma_R^+ + 0.69\sum_{X,Y}\sigma_I - 0.27 \qquad (1)$$

Table I. Relative Reactivities of Alkenes Toward Carbenic Species at 25°

Alkene	C_6H_5CBr		C_6H_5CCl		C_6H_5CF		CH_3SCCl	
	carbenoid[a]	carbene[b]	carbenoid[c]	carbene[d]	carbenoid[e]	carbene[f]	no crown[g]	crown[h]
$Me_2C{=}CMe_2$	1.6	4.4	2.6	5.1	2.7	5.8_5	7.4_5	7.6
$Me_2C{=}CHMe$[i]	1.3	2.5	1.6	3.2	1.2	3.0	1.9	2.1
$Me_2C{=}CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
c-MeCH=CHMe[i,j]	0.29	0.53	0.31	0.37	0.12	0.28	0.29	0.25
t-MeCH=CHMe[j]	0.15	0.25	0.11	0.20	0.10	0.20_5	0.21	0.19
m_{CXY}^{obsd}	0.59	0.70	0.75	0.83	0.87	0.89	0.88	0.93

[a] ($C_6H_5CHBr_2$ + KO-*t*-Bu), ref. 10. [b] ($C_6H_5CBrN_2$ + *h*ν), ref. 11. [c] ($C_6H_5CHCl_2$ + KO-*t*-Bu), ref. 12 [d] ($C_6H_5CClN_2$ + *h*ν), ref. 12. [e] (C_6H_5CHBrF + KO-*t*-Bu), ref. 4. [f] Same as *e*, *with 18-crown-6*; this work. [g] (CH_3SCHCl_2 + KO-*t*-Bu); this work. [h] Same as *g*, *with 18-crown-6*; this work. [i] Relative reactivities are composites of *syn*-halo and *anti*-halo modes of carbene addition. [j] Additions are stereospecific with regard to alkene geometry.

The following observations and interpretations derive from Table I. (1) Relative reactivities for CH_3SCCl additions are essentially identical, whether 18-crown-6 is or is not present during its generation. The "crown ether test"[2] thus establishes CH_3SCCl to be a free carbene when generated by butoxide-induced α-elimination.[13a] (2) C_6H_5CF is not free when so generated. However, the free carbene can be obtained by the crown ether method,[13b] a valuable result because a diazo precursor is unavailable. (3) C_6H_5CX carbenoids exhibit *lower selectivities* than the corresponding carbenes. We attribute this to the presence of K^+Hal^- in the carbenoid addition transition states, resulting in greater charge dispersal (*vis-à-vis* the analogous carbene addition transition states). This leads to less positive charge localization on the alkenic carbons, and to a "damped" discrimination between alkenes.[8] (4) More speculatively, selectivity differences between these carbenoids and carbenes apparently narrow as the carbenic species become more selective; similar selectivities are seen for the C_6H_5CF species,[14,15] and, with CH_3SCCl, only one species is kinetically detected.[14,16]

If selectivity (at least partly) reflects "internal stabilization"[17] of a carbene, then observation (4) suggests that carbenes as or more selective than CH_3SCCl ($m_{CXY} > 0.91$)[18] may be sufficiently stabilized by their substituents to be free even when generated in the presence of K^+Hal^- or K^+OR^-. CCl_2 ($\underline{m} = 1.0$), for example, appears to be free when generated in the presence of KOR,[19] whereas C_6H_5CX ($\underline{m} < 0.9$) are not (Table I). This tandem application of crown ether complexation and $\underline{m}_{CXY}$ analysis to problems of carbenic reactivity simplifies and orders heretofore confusing and unrelated data. It is also powerfully suggestive of new experiments which are in progress.

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(7) Satisfactory characterization by spectral and analytical methods has been completed, and will appear in a full paper.

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(9) For ease of analysis, the chloromethylthiocyclopropanes were *quantitatively* oxidized (with *m*-chloroperbenzoic acid) to the corresponding sulfones[7] prior to gc.

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(13)(a) This conclusion refers to the cyclopropanating species. A similar application of the crown ether test to dimethylmethylene carbene has been reported by P. J. Stang and M. G. Mangum, J. Am. Chem. Soc., 97, 1459 (1975); note 20. (b) Based upon our demonstration[2] of equivalence between photogenerated and KOR-18-crown-6 generated C_6H_5CBr (and C_6H_5CCl).

(14) We take ± 0.03 to be experimental error in $\underline{m}_{CXY}^{obsd}$.

(15) $\underline{m}_{C_6H_5CF}^{calc}$ [from eq. (1)] is 0.96, which differs from $\underline{m}_{C_6H_5CF}^{obsd}$ by ~0.07. This is reasonable agreement, given that the average deviation of the differences between $\underline{m}_{CXY}^{calc}$ and m_{CXY}^{obsd} is ± 0.05,[3] and that $\underline{m}_{C_6H_5CF}^{obsd}$ was not included in the regression analysis which defined the parameters of eq. (1).[3]

(16) $\underline{m}_{CH_3SCCl}^{calc}$ cannot be obtained from eq. (1) because $\sigma_{\underline{R}}^{+}(CH_3S)$ is a reaction-dependent variable: S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, Prog. Phys. Org. Chem., 10, 1 (1973), cf., pp. 40-41. Taking $\underline{m}_{CH_3SCCl}^{obsd}$ ~0.91 (Table I), one can calculate from eq. (1) that $\sigma_{\underline{R}}^{+}(CH_3S)$ ~ -0.39 in the addition of CH_3SCCl to alkenes. The significance of this "high" value will be discussed in our full paper.

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(18) This value is offered as a rule of thumb. Given the imprecision in $\underline{m}$,[14,15] the "critical zone" for the carbenoid-carbene transition might be taken as ~$0.85 < \underline{m} < 0.95$.

(19) Reference 8, pp. 287-288, and citations therein.