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THE OLEFINIC SELECTIVITY OF DIBROMOCARBENE

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The selectivities toward olefins of CBr_2[2] and CCl_2[3] were first determined nearly two decades ago, initiating many similar studies of other carbenes.[4] Attempting to correlate the selectivity of CBr_2 with that of CCl_2, Doering and Henderson noted two anomalies in the behavior of CBr_2.[3] They reported: (a) When $\log(\underline{k}/\underline{k}_0)_{CBr_2}$ was "plotted against the comparable dichlorocarbene reactivities the scatter about a hypothetical line (was) so large that no slope (could) be determined," and (b) "...relatively dibromocarbene reacts slower than dichlorocarbene, the greater the degree of substitution. This falling off may indicate the operation of a steric factor."[3] In particular, CBr_2 was observed to add more slowly to tetramethylethylene than to trimethylethylene (rel. react. = 0.93),[3] a result which has been taken as an archetypical example of steric hindrance in a carbene addition reaction.[5]

Our interest in the correlation of carbenic selectivity,[6] together with the availability of new methods for the differentiation of carbene and carbenoid addition reactions,[7] led us to reinvestigate the olefinic discrimination of CBr_2. The results, which follow, importantly revise our picture of CBr_2 selectivity.

Dibromocarbene was generated by the action of KOR on $CHBr_3$, and added to the olefins enumerated in the Tables. The product cyclopropanes, isolated by gc, were characterized by ir, nmr, and mass spectroscopy. Satisfactory exact mass spectral analyses were obtained for new compounds. Carbenic selectivities (25°) were determined by the olefin competition method,[2-4] in which binary cyclopropane product mixtures resulting from pairs of competing olefins were analyzed by gc (calibrated detector). Relative reactivities were calculated in the standard manner;[3,4] the average deviation from the mean of duplicate experiments was generally $<2\%$, and satisfactory cross-checks[3,4] were obtained.

To delineate the role of carbenoids[7] in the CBr_2 additions, most of the competitions were performed both with and without an added equivalent of 18-crown-6.[8] And, because CBr_2 could convert $\underline{t}$-butoxide to isobutene,[9] biasing relative reactivities measured against isobutene, $KOC(C_2H_5)_3$ was used as the generative base in all competitions involving isobutene. $KOC(CH_3)_3$ was used in most other situations. Final CBr_2 relative reactivities for di- through tetrasubstituted olefins appear in Table IA, together with analogous data for CCl_2.[10] Reactivity data for CBr_2 and CCl_2[11] additions to monosubstituted olefins appear in Table IB.

Table I. Relative Reactivities of Alkenes Toward Carbenes (25°).

Alkene	CBr_2[a]		CCl_2[b]
	No crown	Crown	
(A) Tetramethylethylene	4.4	4.0[c]	8.98
Trimethylethylene	2.8	2.6	3.12
Isobutene	1.00	1.00	1.00
cis-Butene	0.76	0.44[d]	0.27
trans-Butene	0.43	0.35	0.18
(B) 1-Butene	1.00[e]	1.00	1.00[f]
i-Propylethylene	0.44	0.43	0.48[f]
t-butylethylene	0.037	g	0.051[f]

[a] From $CHBr_3$ + KOR; see text. Benzene was present in the 18-crown-6 runs. [b] From $CHCl_3$ and KOR; see text and refs. 4, 10, and 11. 18-Crown-6 was not used; the CCl_2 is considered to be free under these conditions.[7a] [c] The same value was obtained using 2 equiv. of 18-crown-6. [d] A similar value (0.48) was obtained using $KOC(C_2H_5)_3$, solubilized by THF, in the *absence* of 18-crown-6. [e] $(k_{1\text{-butene}}/k_{cis\text{-butene}})_{CBr_2} = 0.096$. Therefore, to put the monosubstituted olefins on the isobutene scale, multiply by 0.073. [f] Results were similar with 3 generative systems: $CHCl_3$ + $KOC(CH_3)_3$ in benzene; $CHCl_3$ + $KOC(C_2H_5)_3$ in benzene; $CHCl_3$ + $KOC(C_2H_5)_3$ in THF (homogeneous). [g] A poor yield was obtained. The non-crown rate, 0.037, is therefore used below. Note, however, that a satisfactory (non-crown) cross-check [$k_{isopropyl}/k_{t\text{-butyl}}$ = 11.7 (obsd.), 11.6 (calcd.)] connects the (crown) *i*-Pr and (non-crown) *t*-Bu relative reactivities.

Inspection of the CBr_2 results reveals minimal kinetically-effective carbenoid involvement in the $CHBr_3$ - KOR reaction; only with *cis*-butene are the crown and non-crown rates significantly different. Moreover, the steric discontinuity observed earlier[3] is not apparent, tetramethylethylene > trimethylethylene. A good correlation (r=0.995) of $\log(k_i/k_o)_{CBr_2}$ (crown values) *vs*. $\log(k_i/k_o)_{CCl_2}$ for the standard alkenes of Table IA is obtainable, and appears in Fig. 1. CBr_2 appears to be "well-behaved", at least under the present conditions; its selectivity index,[6] $m^{25°}_{CBr_2} = 0.65$.

Absence of a discontinuous steric effect does not preclude the operation of all differential steric effects. Thus, $m^{obsd}_{CBr_2}$ (0.65) is significantly lower than $m^{calcd}_{CBr_2}$ (0.82), given by a refined version (9 carbenes)[12] of our dual substituent parameter equation.[6] This discrepancy could reflect *continuous* steric hindrance to CBr_2 addition, which would oppose and level electronic selectivity based upon the degree of substrate alkylation. Relevant experiments are presented in Table IB, and in Fig. 2, which correlates the relative reactivities of CBr_2 and CCl_2 toward $RCH{=}CH_2$ with E_s, the steric substituent constants of the alkyl groups.[13] We observe $\delta_{CBr_2} = 0.98$, $\delta_{CCl_2} = 0.88$, or $\delta_{CBr_2}/\delta_{CCl_2} = 1.11$. This can be taken as a measure of the relative susceptibility of CBr_2 to steric hindrance during these additions. In a suggestive numer-

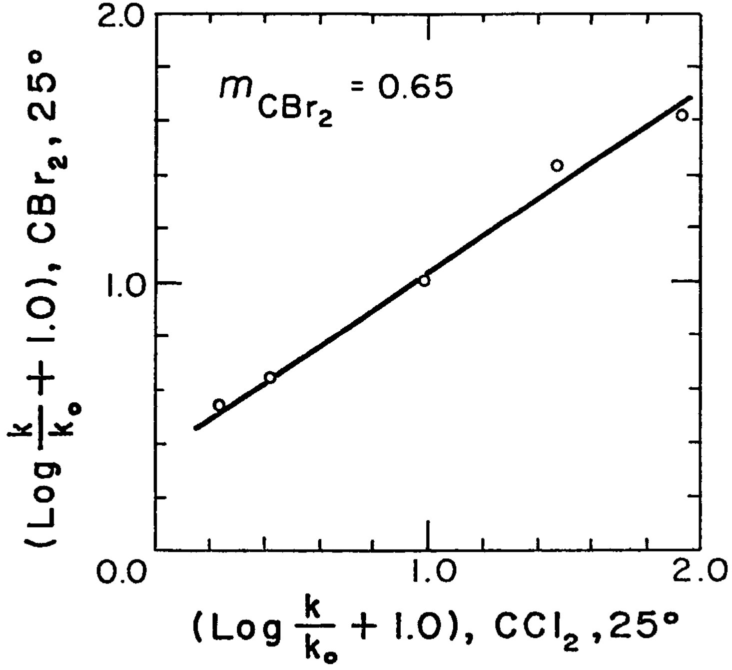

Figure 1. Log(k/k_o) for CBr_2 vs. log(k/k_o) for CCl_2, at 25°. Relative rates were multiplied by 10. The correlation coefficient is 0.995. From left to right, the olefins are trans-butene, cis-butene, isobutene (standard), trimethylethylene, and tetramethylethylene. See Table IA and text.

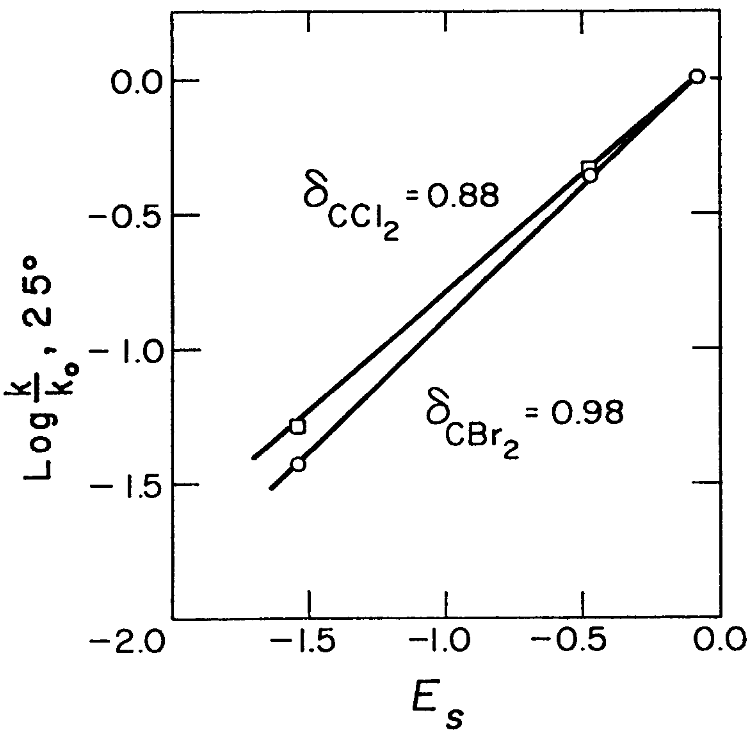

Figure 2. Log(k/k_o) for CBr_2 (circles) and for CCl_2 (squares) vs. steric substituent constants, E_s. The correlation coefficients are 0.9996 and 0.9998, respectively. From left to right, along each line, the olefins are t-butylethylene, i-propylethylene, and 1-butene (standard). See Table IB and text.

ical experiment, (crown) CBr_2 reactivities (Table IA) were altered arbitrarily by 11% (the relative steric susceptibility[14]) in the direction of greater selectivity. The artificially enhanced reactivities afforded $\underline{m}'_{CBr_2} = 0.72$. A small explicit steric correction can thus substantially narrow the gap between $\underline{m}^{obsd}_{CBr_2}$ and $\underline{m}^{calcd}_{CBr_2}$. In principle, relative steric susceptibilities could be measured for many carbenes and explicitly included in the selectivity correlation equation.[15]

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References and Notes

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(5) R. A. Moss, in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970 pp. 35ff. Note, that Skell and Garner[2] found CBr_2 slightly more reactive toward tetramethylethylene than trimethylethylene (rel. react. = 1.1). Their product analyses were carried out by fractional distillation, however, a less precise technique than gc (used by all later investigators).

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(11) For analogous CCl_2 reactivities at -10°, cf. R. A. Moss and A. Mamantov, Tetrahedron Lett., 3425 (1968).

(12) $\underline{m}_{CXY} = -1.10\sum_{X,Y}\sigma^+_{\underline{R}} + 0.53\sum_{X,Y}\sigma_{\underline{I}} - 0.31$; C. B. Mallon, Ph.D. Thesis, Rutgers University, 1976.

(13) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, pp. 556ff.

(14) The relative steric hindrance to CBr_2 addition might be larger than 1.11 were it determined with tri- or tetrasubstituted olefins, instead of the monoalkylated substrates used here.

(15) A referee requested that we comment on the divergence between our relative reactivity results and those of previous[3] investigators. Our experimental conditions differ in temperature, solvent, choice of standard olefin, and, not least, in nearly two decades of improvement in gc facilities. It would therefore be extremely difficult to trace the origin of the discrepancies, and we have not endeavored to do so; indeed, we have avoided deliberate repetition of the earlier work. The important point is that, under our "standard" conditions, CBr_2 appears to be as "well-behaved" as other carbenes, and that this has certain clear consequences for the study of carbene chemistry.

We have also been asked why the crown ether results differ from the non-crown results only in the cis-butene case. Other than to indicate that both sets of data are reproducible, we have no publishable explanation for this curious finding.