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STERIC HINDRANCE IN THE ADDITION OF DICHLOROCARBENE TO OLEFINS

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A recent reactivity comparison of dichlorocarbene and chlorofluorocarbene suggested that steric hindrance played an important role in determining the rate of the carbene-olefin addition reaction (1). Indeed, although warnings were issued early during the carbene renaissance (2), Seyferth could still say, in 1967, "for these CCl_2 transfer systems...steric effects are of some importance, a fact not generally appreciated." (3) Thus, although occasional references to steric hindrance to carbene addition can be found in the literature, emphasis is more generally placed on electronic effects. With regard to dichlorocarbene, steric hindrance has been implicated in its "failure to add to the Δ^{5}-double bond of Δ^{5} or $\Delta^{3,5}$-steroids bearing a 10β-methyl group" (4), in its addition only to the cyclopentene double bond of endo-dicyclopentadiene (5); and in its stereospecific addition to 3-deoxy-1,2:5,6-di-O-isopropylidene-α-D-erythro-hex-3-enofuranose (6).

The only attempt at a systematic, quantitative study of steric hindrance to dichlorocarbene addition seems to be that of Bezaguet and Bertrand, who determined the relative rates of addition of dibromo and dichlorocarbene to a series of 1-alkyl-1-methylallenes (7). We thought it worthwhile to determine analogous data for a series of 1-alkylethylenes, since such data could be more easily extrapolated to that large body of work concerned with structure-reactivity variation in the carbene-alkene addition reaction. The results demonstrate that steric effects are as important as electronic effects in controlling the rate of addition of dichlorocarbene to simple alkenes; a point which has, for too long, lacked emphasis in the literature.

Dichlorocarbene was generated by the action of potassium <u>t</u>-butoxide on chloroform at -10°, and added to $RCH{=}CH_2$; R=ethyl, i-propyl, t-butyl, n-butyl, i-butyl, and neo-pentyl. The product 1,1-dichloro-2-alkylcyclopropanes were isolated in fair yield and purified by gas chromatography. They were characterized by satisfactory infra-red and NMR spectra, and by elemental analysis.

The olefins were then allowed to compete, in pairs, for dichlorocarbene, and relative rates for the carbene addition reaction were determined from the product mixtures in the standard manner (2). Analysis of the product mixtures was carried out by gas chromatography on either a 12', 0.25", SF-96 packed column, or on a 100' SF-96 Golay column. In both cases the detector was calibrated with prepared mixtures of pure cyclopropanes. The data is gathered in Table 1.

Table 1

Relative Rates of Addition of Dichlorocarbene to $RCH{=}CH_2$ at -10°

R_1/R_2	k_1/k_2	av. dev.₂
i-C_4H_9/n-C_4H_9	0.80	0.02
neo-C_5H_{11}/i-C_4H_9	0.98	0.01
i-C_3H_7/t-C_4H_9	14.6	0.3
C_2H_5/i-C_3H_7	2.34	0.01
i-C_3H_7/i-C_4H_9	0.43	0.02

The data can be adjusted to a 1-butene standard, and are so displayed in Table 2.

The data are not correlated by the Taft polar-steric relation, $\log (k/ko) = \sigma^* p^* + \delta E_S$ (8). Examination of the data suggests a natural separation into two groups. Along the series R=ethyl, i-propyl, t-butyl, corresponding to successive methylations at the α carbon of the alkyl substituent, there is sharp rate reduction. On the other hand, along the series R=n-butyl, i-butyl, neo-pentyl, corresponding to successive methylations at the β carbon of the alkyl substituent,

Table 2

Rates of Addition of Dichlorocarbene to $RCH{=}CH_2$,
Relative to 1-Butene, -10°

R	Relative Rate
C_2H_5	1.00
i-C_3H_7	0.43
t-C_4H_9	0.029
n-C_4H_9	1.24
i-C_4H_9	0.99
neo-C_5H_{11}	0.97

there is only a mild and unexceptional trend. The first group of data is well correlated by steric substituent constants, $\log(k/ko) = \delta E_S$, (8), with δ about 1.0. The second group of data is not correlated by the line so defined.

Steric hindrance is an important factor in controlling the rate of carbene addition to even the most simple olefins. The decrease in rate effected by α-alkylation of olefinic substituents can be greater than the increase in rate effected by alkylation of the olefinic carbons themselves. For example, successive methylation of isobutene to tetramethylethylene increases the rate of dichlorocarbene addition by only a factor of 6.5 (2), while successive α-methylation of 1-butene to t-butylethylene decreases the rate of dichlorocarbene addition by a factor of 34.5. Adverse steric factors presumably cut down the rate enhancements obtainable by alkylation of the olefinic carbon atoms.

Furthermore, the steric effects are specific, since only alkylation of the α carbon and not the β carbon of the olefinic alkyl group leads to substantial rate reductions. That the rate data for α methylation is correlated by steric substituent constants lends weight to the belief that the observed rate reductions are indeed steric in origin, and not due to loss of hyperconjugative resonance in the addition reaction transition state, as α protons are replaced by methyl groups.

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