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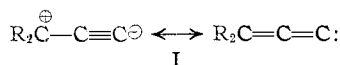
The Stereochemistry and Relative Rates of Addition of Dimethylvinylidene Carbene to Olefins

BY H. D. HARTZLER

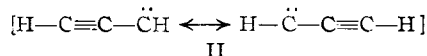
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Dimethylvinylidene carbene, obtained from 3-chloro-3-methyl-1-butyne and base, has been added in a stereospecific manner to *cis*- and *trans*-2-butene. The carbene has been allowed to react with pairs of olefins. Analysis of the relative amounts of the two alkenylidenecyclopropanes formed gives the relative rates of addition of the carbene to the olefins. The data show that dimethylvinylidene carbene is an electrophilic species which has a selectivity in olefin additions approximately that of dibromomethylene.

Evidence for the formation of alkenylidene carbenes has been obtained from a study of the kinetics of reaction of tertiary acetylenic halides with bases¹ and from the synthesis of alkenylidenecyclopropanes.² The alkenylidene carbenes have been represented by the resonance hybrid I.^{1,2} This is an



unusual structure for divalent carbon intermediates, for if the dipolar structure makes an appreciable contribution to the resonance hybrid, the electrophilic character of carbenes in the singlet state³⁻⁶ may be diminished. The only other unsaturated carbenes which have been studied to date exhibit unusual behavior. Propargylene⁷ (II) appears to react as though it were a free radical, and vinyl carbenes⁸ undergo an intramolecular addition reaction to form cyclopropenes.

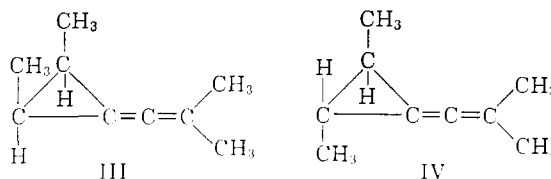


If I is a satisfactory representation of the structure of the alkenylidene carbenes, it is to be expected that they would add stereospecifically *cis* to olefins; for non-stereospecific addition appears to be characteristic of carbenes with unpaired electrons.^{7,9} The measurement of relative reactivities of carbenes toward olefins has previously been shown³⁻⁶ to provide a convenient measure of the selectivity of the carbene and thus to give information on the stabilization of the carbene by substituents. This paper gives the results of a study of the stereochemistry and relative rates of the reaction of methylpropenylidene carbene (I, R = CH₃) with olefins.

Results

The reaction of methylpropenylidene carbene with olefins was shown to result in stereospecific addition. The addition of 3-chloro-3-methyl-1-

butyne to a slurry of potassium *t*-butoxide in *cis*-2-butene produced 1-(2-methylpropenylidene)-*cis*-2,3-dimethylcyclopropane (III). A similar reaction with *trans*-2-butene gave the *trans* isomer IV.



Analysis of the reaction products by vapor phase chromatography (v.p.c.) showed that no detectable amount of IV was present in the product derived from *cis*-2-butene, while only a trace (<1%) of III was found in the product from *trans*-2-butene. It is believed that this arose from the small amount of *cis*-2-butene present in the starting material. The configurations of III and IV have not been proved rigorously. They appear to be the more reasonable assignments because of the higher boiling point and refractive index of the *cis* isomer and because of the conceptual difficulties of a stereospecific *trans* addition in a carbene reaction.¹⁰ A rigorous proof of a *cis* addition of a carbene to an olefin has recently appeared.¹¹

The relative rates of the olefin addition reactions can be determined by allowing the carbene to react with pairs of olefins. When the olefins are present in large excess, when the products are formed by reactions of the same kinetic order and when the products are not consumed under the reaction conditions, rate ratios may be obtained from product ratios as given by eq. 1

$$k/k_0 = P/P_0 \times O_0/O \quad (1)$$

where P = mole fraction of product and O = mole fraction of olefin.

The first condition was met by using a tenfold excess of each olefin, the second condition was assumed to be true and the third condition is known not to be true and introduces error into our data. The products are allenes and do react with the carbenes, although use of the large excess of olefin minimizes this reaction under the competitive conditions and allows us to attach quantitative significance to the results.

(10) The proton nuclear magnetic resonance spectra of III and IV, while completely consistent with the structural assignments, did not permit us to make unequivocally the stereochemical assignments.

(11) W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(1) G. F. Henion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951).

(2) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

(3) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(4) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(5) P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1958).

(6) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960).

(7) P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960).

(8) G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003 (1961); **83**, 2015 (1961).

(9) R. M. Etter, H. S. Skovronek and P. S. Skell, *ibid.*, **81**, 1008 (1959).

TABLE I
RELATIVE RATES OF ADDITION OF CARBENES TO OLEFINS

Olefin	$(\text{CH}_3)_2\text{C}=\text{C}=\text{C}$	CCH_3^a	$\log (k/k_0)$ CBr_2^a	CHCl_2^c	$\text{CHCO}_2\text{C}_2\text{H}_5^d$
2,3-Dimethyl-2-butene	1.3	1.73	0.84	0.67	0.21
2-Methyl-2-butene	0.67	1.37	.87	.47	.21
2-Methyl-1-butene	.70	0.74			
Cyclohexene	.00	.00	.00	.00	.00
1-Hexene	-.80	-.73	-.71 ^b		
1-Pentene		-.86	-.78	-.42	-.04

^a Data of Doering and Henderson.⁴ ^b Data of Skell and Garner³ adjusted to cyclohexene as standard. ^c Data of Closs and Schwartz⁶ adjusted to cyclohexene as standard and including rates of formation of both *cis* and *trans* isomers. ^d Data of Skell and Etter⁵ adjusted to cyclohexene as standard and given as logarithms.

The competition experiments were run between -10 and 0° . 3-Chloro-3-methyl-1-butyne was added to an equimolar amount of potassium *t*-butoxide in a tenfold excess of each olefin. The reaction mixtures were filtered, and the crude filtrates were analyzed by v.p.c. The relative rates were calculated from eq. 1. The olefins were measured in competition with cyclohexene which was used as a standard and assigned a relative rate of one. Our results, given as the logarithms of the relative rate constants, are given in Table I, along with similar data obtained for other carbenes. Our results are the average of duplicate or triplicate runs which were in agreement within 10%.

Discussion

The stereospecificity of alkenylidenecyclopropane formation is in agreement with the expected properties of the carbene I. Stereospecificity of addition of carbenes to olefins has been suggested to be a suitable criterion for assigning structures to the carbenes with no unpaired electrons.^{3,12} Additional support for the argument has been obtained by the observation of typical radical reactions of diphenylmethylene¹³ which adds non-stereospecifically to olefins.⁹ No radical reactions have been observed for I.

The competition experiments show clearly that I reacts most readily with the most highly substituted olefins. The identical rates of reaction of I with 2-methyl-2-butene and 2-methyl-1-butene are exceptions to this statement, but they do not obscure the over-all trend.¹⁴

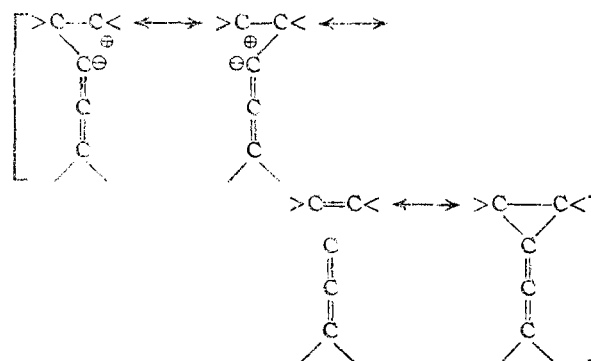
The general behavior is that expected of an electrophilic reagent and parallels the results obtained for the other carbenes given in the table. The yields of alkenylidenecyclopropanes² also increase with increased substitution of the olefin, indicating that the olefin competes with the alkoxide ion for the carbene. The response of the rates of addition of I to olefin structure suggests that in the transition state of the reaction, electrical charge is removed from the olefin to the carbene.

The differences in reactivity of I with olefins are large in comparison with chlorocarbene or carbethoxycarbene, and all of the carbenes in Table I are more selective in attack than is methylene.¹⁵

(12) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(13) W. Kirmse, L. Horner and H. Hoffmann, *Ann.*, **614**, 19 (1955).

(14) A plot of $\log (k/k_0)$ for I versus $\log k/k_0$ for CCl_2 should be linear if steric effects are negligible. A good linear plot is obtained with the exception of the point for 2-methyl-2-butene, in which case our value appears to be about 30% low. No satisfactory explanation for this discrepancy is now available.



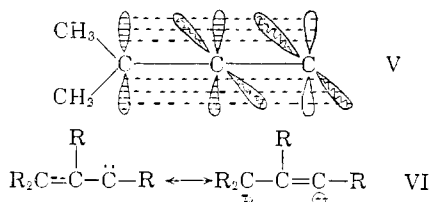
Compound I reacts with 2,3-dimethyl-2-butene 79 times more rapidly than it does with 1-hexene, while the corresponding rate ratios for dichlorocarbene and dibromocarbene are 288 and 35. These reactivity differences may not be wholly attributable to electronic differences. A steric retardation of rate of reaction of dibromocarbene with highly substituted olefins has been suggested previously.⁴ This is readily seen by comparing reactivity differences of dibromocarbene and I. Thus, I appears to be the more discriminate reagent in the competition of 2,3-dimethyl-2-butene and cyclohexene, while dibromocarbene is more discriminate in reaction between cyclohexene and 1-hexene. The steric requirements of I should be the lowest of any of the carbenes in that a nearly naked carbon atom is added to the olefin.¹⁶ The near-linearity of a plot of $\log (k/k_0)$ for I versus $\log (k/k_0)$ for CCl_2 ¹⁴ suggests that steric effects are of little importance in the olefin addition reactions of dichlorocarbene as well as those of I.

Along with the demonstration of the electrophilic nature of the carbenes and the steric requirements in the olefin addition reactions, the data of Table I give an indication of the ability of the carbenes to discriminate in reaction. To the extent that the ability of a carbene to differentiate between reaction paths may be translated into the internal stabilization of the carbene, we can discuss the relative stabilities of I and other carbenes. The increased stability of halocarbenes over methylene has been attributed to overlap of the filled p-orbitals of the halogen with the vacant p-orbital of carbon.³ On this basis, the greater stability of dichlorocarbene over chlorocarbene or dibromocarbene is

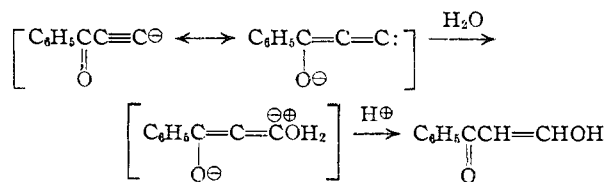
(15) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(16) This statement assumes that the carbene intermediate is linear as written (I). Bent structures are conceivable, even to the extreme case of a cyclic structure, dimethylcyclopropyne, which might react as does I; but these formations appear to be less likely.

readily rationalized. The enhanced stability of I over methylene or alkyl carbenes may be attributable to overlap of the vacant p-orbital with the π -electrons of the β,γ -double bond (V). If this is the case, one can predict that β,γ -unsaturated carbenes (VI) in general will be considerably more stable than methylene.



The reactions of I with nucleophiles are unusual in that attack can occur at either the α - or γ -carbon atom. Thus, I undergoes reaction at the γ -carbon atom with alkoxide ions¹ and with amines¹⁷ to give acetylenic ethers and amines, while it gives reaction at the α -carbon atom with olefins to give cyclopropanes. The choice between reaction paths for I is not simply related to the charge of the nucleophile or its relative nucleophilicity, for I ($\text{R} = \text{C}_6\text{H}_5$) reacts with acetylenic anions at the α -carbon atom to give cumulenes.² The ability of an alkenylidene carbene to react with a hydroxylic solvent at the α -carbon atom has been demonstrated in the formation of hydroxymethyleneacetophenone from the anion of benzoylacetylene.¹⁸ No satisfactory ex-



(17) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

(18) H. D. Hartzler and J. L. Warnell, unpublished work.

planation for the differentiation in reaction paths is available at present, and reactions of I with anions are currently under investigation.

Experimental¹⁹

1-(2-Methylpropenylidene)-*cis*-2,3-dimethylcyclopropane (III).—The allene was prepared by the procedure previously given for the preparation of 7-(2-methylpropenylidene)-bicyclo[4,1,0]-heptane.² *cis*-2-Butene and 3-chloro-3-methyl-1-butyne gave a 23% yield of III, b.p. 80–82° at 66 mm., n_D^{25} 1.4830–1.4835.

Anal. Calcd. for C_9H_{14} : C, 88.45; H, 11.55. Found: C, 88.47; H, 11.66.

1-(2-Methylpropenylidene)-*trans*-2,3-dimethylcyclopropane (IV).—*trans*-2-Butene and the acetylenic chloride gave a 19% yield of IV, b.p. 66–68° at 54 mm., n_D^{25} 1.4792–1.4800.

Anal. Calcd. for C_9H_{14} : C, 88.45; H, 11.55. Found: C, 88.26; H, 11.70.

V.p.c. analysis of the reaction mixtures from *cis*- and *trans*-2-butene showed mainly the one isomer in each case. The analysis of the mixtures was done on the crude product, after filtration but before distillation. No detectable amount of IV was found in the reaction product from *cis*-2-butene. A trace of III was found in the reaction product from *trans*-2-butene. The amount was approximately equal to the amount of *cis*-2-butene present as a contaminant in the starting material. The column employed for analysis was 7 ft. \times 0.25 in. copper tubing packed with Columpak firebrick coated with tris-cyanoethyl glyceryl ether and operated at 102° with a helium flow rate of 40 cm.³/min. The retention time of IV was 4.3 minutes, while III eluted at 6.1 minutes. Separation was complete.

Competition Experiments.—The conditions used were comparable to those used in the preparative experiments.² Mixtures containing 0.10 mole each of cyclohexene and the competing olefin, and 0.010 mole of potassium *t*-butoxide were stirred at -10° under nitrogen. 3-Chloro-3-methyl-1-butyne (1.10 g., 0.010 mole) was added dropwise with the temperature maintained between -10 and 0° . The mixtures were stirred for 5 minutes, pentane (50 ml.) was added, and the mixtures were filtered. The crude filtrates were analyzed by v.p.c. In all cases separations between the two allenics were complete. The column and conditions employed were those used with the products from *cis*- and *trans*-2-butene.

(19) Boiling points are uncorrected.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF LEPETIT S.P.A., MILAN, ITALY]

A New Synthesis of Tropane Derivatives

BY G. CIGNARELLA, G. G. GALLO AND E. TESTA

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A new synthesis of 3α -phenyltropane derivatives has been carried out starting from *cis*-2,5-dicarbethoxypyrrolidine (IV), 8-tosyl- 3β -cyano- 3α -phenylnortropane (VIII) being the intermediate product. 3α -Phenyl- 3β -nortropanecarboxylic acid (XI) and its ethyl ester XIII, 3α -phenyltropane- 3β -carboxylic acid (XII) and its ethyl ester XIV, 3α -phenyl- 3β -nortropanyl phenyl ketone (XVI) and 3α -phenyl- 3β -tropanyl phenyl ketone (XVII) have been synthesized and found identical by chemical and spectral properties with the compounds previously obtained from α -ecgonine.

In connection with a research program directed toward the synthesis of a new class of bicyclic nitrogen compounds, which recently led one of us to the preparation of 3,8-diazabicyclo[3.2.1]octane and many its derivatives,^{1,2} we were able to complete from suitable intermediates³ a new synthesis

(1) G. Cignarella and G. G. Nathansohn, *J. Org. Chem.*, **26**, 1500 (1961).

(2) G. Cignarella, G. G. Nathansohn and E. Occeili, *ibid.*, **26**, 2767 (1961).

(3) G. Cignarella and G. G. Nathansohn, *Gazz. chim. ital.*, **90**, 1495 (1960).

