Polar Selectivity of Carbene Addition to 3-Substituted Propenes

By **Toshihiko Migita,* Kiyoshi Kurino,** and **Wataru Ando,** Faculty of Engineering, Gunma University, Tenjin-cho Kiryu, Gunma, Japan

Relative rate constant for the addition of several carbenes to a series of allylic compounds have been determined by means of competititive experiments. These results and derived Hammett–Taft parameters show that polar selectivities of carbenes are generally low, but correlate with the polar natures of the carbene substituents. The selectivity of a singlet carbene was even lower than that of the corresponding triplet state. These facts support a mechanism of addition of singlet carbene involving a transition state having only a slight contribution from polar structures. Low selectivities of alkoxycarbonylcarbenes suggest that the $-R$ effects of the alkoxycarbonyl groups do not affect the addition reactivities of the carbenes.

THERE have been many studies on selectivities of addition of carbenes to olefins. The data have been reviewed with regard to the relationship between reactivity and structure of the substrate and the carbene.[1] Selectivities of the reactions of halogenocarbenes have been most extensively studied, and the $+R$ effect of the halogen substituents has been demonstrated in that the ρ value for addition of difluorocarbene to substituted

---

[1] R. A. Moss, ' Carbenes,' vol. I, ed. M. Jones, jun., and R. A. Moss, Wiley, New York, 1973, ch. 2.

styrenes has been found less negative than that of dichlorocarbene.[2] Conversely, the effect of $-R$ delocalization of a lone-pair at the carbene site would be expected to impart electrophilic selectivity to the carbene, as shown by the notably electrophilic character of cyclopentadienylidene (ρ -0.47).[3]

Bismethoxycarbonylcarbene has been found slightly more selective than methoxycarbonylcarbene in addition to olefins as well as in C–H insertion reactions, and the extra selectivity has been ascribed to extra resonance stabilisation due to the $-R$ effect of the alkoxycarbonyl group.[1] If this π-delocalization effect operates in the addition reactions of bisalkoxycarbonylcarbenes, the polar selectivity in addition would be expected to be larger than that of dichlorocarbene, as judged from the fact that Hammett σ_p constants of alkoxycarbonyl substituents are more positive than that of a chloro-substituent. However, few quantitative data on the polar selectivities of alkoxycarbonylcarbenes are available.

Another point of interest in the reactions of alkoxycarbonylcarbenes is that it is possible to compare addition selectivities a singlet carbene and the corresponding triplet carbene, since either singlet or triplet alkoxycarbonylcarbenes can be generated almost exclusively from the corresponding diazo compounds by direct or benzophenone-sensitized photolysis, respectively.[4] We first attempted to study the addition of these carbenes to substituted styrenes, because the triplet carbene was expected to show a unique selectivity similar to that of radical addition, as demonstrated in the reaction of trichloromethyl radical with substituted styrenes.[5] Unfortunately, however, experimental conditions affording reproducible results were not found, presumably owing to difficulties resulting from polymerization of the styrenes.

In this paper, polar selectivities of alkoxycarbonylcarbenes in additions to allylic substrates are compared with those of dichloro- and phenyl-carbenes and cyclopentadienylidene.

RESULTS AND DISCUSSION

Competitive experiments were carried out by generating the carbenes in binary mixtures of the allylic substrates (in *ca.* 30 molar excess). The carbenes were derived from direct or benzophenone-sensitized photolysis of the corresponding diazo-compounds. Relative reactivities of the substrates were calculated from their initial relative concentrations and the molar ratios of the carbene adducts produced (determined by g.l.c.). The results (Table 1) show that the observed values of relative rates are satisfactorily reproducible. Furthermore, these data are self-consistent, *i.e.* values of relative rate constants, k_X/k_Y, estimated indirectly from the several pairs of substrates employed by use of the equation $k_X/k_Y = k_X/k_Z \cdot k_Z / k_Y$ are in good agreement with those determined directly. For example for singlet bismethoxycarbene, $k_{\mathrm{SiMe_3}}/k_{\mathrm{Cl}} = k_{\mathrm{SiMe_3}}/k_{\mathrm{OMe}} \cdot k_{\mathrm{OMe}}/k_{\mathrm{Cl}} = 1.82$, and $k_{\mathrm{OMe}}/k_{\mathrm{Cl}} = k_{\mathrm{Pr}}/k_{\mathrm{Cl}} \cdot k_{\mathrm{OMe}}/k_{\mathrm{Pr}} = 0.97$ (*cf.* 1.83 and 0.91 obtained directly). Thus were obtained the reactivities of the allylic substrates toward each carbene relative to that of allyl methyl ether (Table 2). The relative reactivity of allyl chloride towards phenylcarbene could not be determined, owing to the instability of the adduct under the conditions of the g.l.c. analysis. For comparison, the relative reactivities of the same substrates towards bromine addition in chloroform solution were also determined.

TABLE 1

Results of competitive reactions

Reagent	Substrate $CH_2{=}CH{\cdot}CH_2X$	$CH_2{=}CH{\cdot}CH_2Y$	k_X/k_Y
Singlet :CHCO$_2$Me at 18 °C	SiMe$_3$	Cl	2.07 ± 0.04
	SiMe$_3$	OMe	1.65 ± 0.08
	Pr^n	Cl	1.47 ± 0.02
	Pr^n	OMe	1.22 ± 0.01
	CN	Pr^n	0.63 ± 0.06
	CN	Cl	1.00 ± 0.04
Triplet :CHCO$_2$Me at 18 °C	SiMe$_3$	Cl	2.55 ± 0.02
	SiMe$_3$	OMe	2.68 ± 0.06
	Pr^n	Cl	1.55 ± 0.01
	CN	Cl	0.66 ± 0.03
Singlet :C(CO$_2$Me)$_2$ at 18 °C	SiMe$_3$	Cl	1.83 ± 0.06
	SiMe$_3$	OMe	2.00 ± 0.03
	Pr^n	Cl	1.53 ± 0.06
	Pr^n	OMe	1.57 ± 0.04
	OMe	Cl	0.91 ± 0.07
	CN	OMe	1.22 ± 0.02
Triplet :C(CO$_2$Me)$_2$ at 18 °C	SiMe$_3$	Cl	3.66 ± 0.08
	SiMe$_3$	OMe	2.92 ± 0.04
	Pr^n	Cl	2.16 ± 0.01
	CN	Cl	0.80 ± 0.02
:CH at 18 °C	SiMe$_3$	OMe	1.13 ± 0.04
	Pr^n	OMe	1.06 ± 0.04
	CN	OMe	0.92 ± 0.04
Cyclopentadienylidene at 18 °C	SiMe$_3$	Pr^n	1.11 ± 0.04
	SiMe	OMe	1.66 ± 0.06
	OMe	Cl	1.20 ± 0.06
	CN	Pr^n	0.42 ± 0.01
Br$_2$ at 1.5 °C	Pr^n	Cl	164 ± 20
	Pr^n	OMe	56 ± 4
	CN	Cl	0.13 ± 0.03

Good linear free energy relationships were observed between the relative reactivities thus obtained and σ^* substituent constants, except for the reaction of singlet bismethoxycarbonylcarbene. Reaction constants ρ^* and correlation coefficients r are also shown in Table 2.

Although all carbenes studied showed electrophilic tendencies in their addition reactions, the selectivity of carbene addition, giving cyclopropane derivatives, is much lower than that of bromine addition, a typical electrophilic reaction involving formation of bridged bromonium ions. Curiously, relative rate data for addition of singlet bismethoxycarbonylcarbene did not obey a simple linear free energy relationship. For example, the reactivity of allyl cyanide was higher than would be expected from the normal electronic influence of the cyano-group. The reasons for the deviation are not clear. Other paths leading to the cyclopropane deriva-

---

[2] R. A. Moss and C. B. Mallon, *J. Amer. Chem. Soc.*, 1975, **97**, 344.

[3] H. Durr and F. Werndorff, *Angew. Chem.*, 1974, **86**, 413.

[4] M. Jones, jun., W. Ando, M. E. Hendrick, A. Kulczycki, jun., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Amer. Chem. Soc.*, 1972, **94**, 7469.

[5] H. Sakurai, S. Hayashi, and A. Hosomi, *Bull. Chem. Soc. Japan*, 1971, **44**, 1945.

TABLE 2

Relative reactivities of the propenes $CH_2{=}CH{\cdot}CH_2X$ towards carbenes [a]

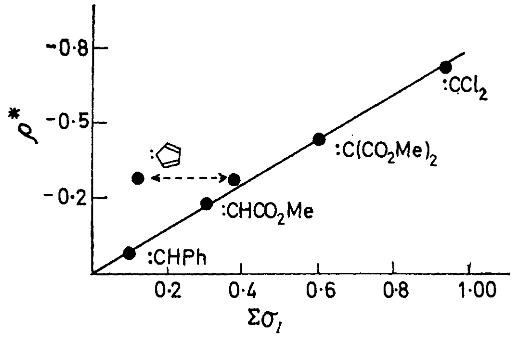
Carbene	Temp. (°C)	X $SiMe_3$	 Pr^n	 OMe	 Cl	 CN	ρ^*	r
$:CH{\cdot}CO_2Me$ (s)	18	1.65	1.22	1.00	0.81	0.77	−0.18	0.993
$:CH{\cdot}CO_2Me$ (t)	18	2.68	1.63	1.00	1.05	0.69	−0.30	0.919
$:C(CO_2Me)_2$ (s)	18	2.00	1.57	1.00	1.09	1.22	−0.36 [b]	
$:C(CO_2Me)_2$ (t)	18	2.92	1.73	1.00	0.80	0.64	−0.37	0.991
$:CHPh$	18	1.13	1.06	1.00		0.92	−0.05	0.999
Cyclopentadienylidene	18	1.66	1.49	1.00	0.83	0.63	−0.25	0.996
Br_2	1.5		56.0	1.00	0.34	0.04	−2.01	0.98

[a] Reactivity of allyl methyl ether toward each reagent taken as unity. [b] Calculated from the relative rate data for the substrates with X = $SiMe_3$, Pr^n, and OMe.

tives might exist.* Nevertheless, polar selectivity in addition reactions of this carbene is apparently small, the ρ^* value estimated from relative reactivities of allyltrimethylsilane, hex-1-ene, and allyl methyl ether being −0.36.

On the basis of stereochemical characteristics,[7] the mechanism of addition of triplet carbenes has been presumed to be a stepwise process, involving radical addition followed by coupling of the resulting diradical. Triplet methoxycarbonyl- and bismethoxycarbonylcarbenes showed small electrophilic selectivity. The ρ^* values observed are of magnitudes similar to those commonly observed in additions of free radicals bearing electronegative groups.[8]

Singlet carbenes, whose electrophilic characteristics are well demonstrated, *e.g.* in ylide formation, are even less electrophilic in these reactions than the corresponding triplet states. These low selectivities are not in conflict with an addition mechanism involving almost synchronous formation of two C–C bonds, which has been presumed from the stereospecific features of the addition.[7]



Substituent effects on carbene polar selectivities (for $:CCl_2$, $\rho^* = -0.74$) [9]

Singlet bismethoxycarbonylcarbene is less selective than dichlorocarbene, the ρ^* value of which has been reported [9] to be −0.74. This suggests that in addition reactions the availability of the lone electron pair of bismethoxycarbonylcarbene is not reduced by the $-R$ effect of the methoxycarbonyl groups, and the transition states for addition of these singlet carbenes have only slight charge separation due to the inductive effects of the groups on the carbene site. This is supported by the simple linear correlation (Figure) between the ρ^* values for phenyl-, methoxycarbonyl-, bismethoxycarbonyl- and dichloro-carbenes and the sum of σ_I constants of the carbene *C*-substituents.

Cyclopentadienylidene in contrast appears markedly electrophilic in these reactions. This might be due to the importance of the 'aromatic' character of cyclopentadienylidene; if so, the point for the carbene would be expected to deviate from the straight line in the Figure. Unfortunately, however, inductive electronic influence on the carbene site cannot be estimated exactly. One might expect the value of $\Sigma\sigma_I$ to be intermediate between those for $(MeCH{=}CH)_2C:$ and $(PhCH{=}CH)_2C:$. The σ_I values of $MeCH{=}CH-$ and $PhCH{=}CH-$ are derived from σ^* values of $MeCH{=}CH{\cdot}CH_2-$ and $PhCH{=}CH{\cdot}CH_2$ (0.13 and 0.41, respectively [10]) according to the equation $\sigma_I(X) = 0.45\sigma^*(CH_2X)$. Thus the total inductive effect on the carbene site of cyclopentadienylidene can be estimated as between 0.12 and 0.37. As can be seen in the Figure, the electrophilic selectivity of cyclopentadienylidene is apparently more than would be expected from the ρ^*–$\Sigma\sigma_I$ correlation if the lower limit of $\Sigma\sigma_I$ is used, but the point almost exactly falls on the line if one uses the upper limit. Thus, the electrophilic tendency of cyclopentadienylidene is not necessarily unequivocal evidence for the importance of its 'aromatic' character.

EXPERIMENTAL

Allylic Substrates.—Hex-1-ene and allyl chloride were purified by fractional distillation. Allyltrimethylsilane,[11] allyl methyl ether,[12] and allyl cyanide [13] were prepared by the usual methods and purified by repeated distillation. Purity of substrates was checked by g.l.c.

Carbene Precursors.—Methyl diazoacetate,[14] dimethyl

---

* For example, *via* ylide formation, which is one of the most characteristic features of singlet bismethoxycarbonylcarbene.[6]

[6] W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, 1969, **91**, 2786.

[7] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, ch. 8.

[8] M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1964, **86**, 242.

[9] E. V. Couch and J. A. Landgreke, *J. Org. Chem.*, 1972, **37**, 1251.

[10] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, 1969, p. 1220.

[11] L. H. Sommer, L. J. Tayler, and F. C. Whitemore, *J. Amer. Chem. Soc.*, 1948, **70**, 2872.

[12] W. T. Olson, H. F. Hipsker, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, jun., and L. C. Gibbons, *J. Amer. Chem. Soc.*, 1947, **69**, 2451.

[13] J. V. Supniewski and P. L. Salzberg, *Org. Synth.*, 1941, Coll. Vol. I, p. 46.

[14] N. E. Sarle, *Org. Synth.*, 1963, Coll. Vol. IV, p. 424.

TABLE 3

Analytical and n.m.r. data [a] for the adducts

Reagent	Substrate				
	$CH_2{=}CH{\cdot}CH_2{\cdot}SiMe_3$	$CH_2{=}CH{\cdot}CH_2Pr^n$	$CH_2{=}CH{\cdot}CH_2{\cdot}OMe$	$CH_2{=}CH{\cdot}CH_2Cl$	$CH_2{=}CH{\cdot}CH_2{\cdot}CN$
$:CH{\cdot}CO_2Me$	δ 0.05 (9 H, s, SiMe) 0.32—2.25 (6 H, m) 3.60 (3 H, s, CO_2Me) Reqd. (%) Found (%) C, 58.0 58.05 H, 9.75 9.75	δ 0.45—1.78 (12 H, m) 1.78—2.45 (1 H, m) 3.60 and 3.62 (each 3 H, s, CO_2Me) Reqd. (%) Found (%) C, 69.2 69.0 H, 10.3 10.3	δ 0.73—1.78 (4 H, m) 3.25 (3 H, d, CH_2Cl) 3.17—4.00 (2 H, m) 3.63 (3 H, s, CO_2Me) Reqd. (%) Found (%) C, 58.3 57.9 H, 8.4 8.35	δ 0.72—2.07 (4 H, m) 3.48 (2 H, d, CH_2Cl) 3.67 and 3.70 (each 3, H, s, CO_2Me) Reqd. (%) Found (%) C, 48.5 48.3 H, 6.1 6.05 Cl, 23.85 24.4	δ0.78—2.10 (4 H, m) 2.32—2.77 (2 H, m) 3.66 and 3.70 (each 3 H, s, OMe) Reqd. (%) Found (%) C, 60.4 60.7 H, 6.5 6.6 N, 10.05 10.2
$:C(CO_2Me)_2$	δ 0.08 (9 H, s, SiMe) 0.31—2.08 (5 H, m) 3.69 (6 H, s, CO_2Me) Reqd. (%) Found (%) C, 54.05 53.8 H, 8.25 8.3	δ 0.60—2.05 (12 H, m) 3.68 (6 H, s, CO_2Me) Reqd. (%) Found (%) C, 61.65 61.6 H, 8.45 8.3	δ 0.78—1.67 (2 H, m) 1.77—2.23 (1 H, m) 3.25 (3 H, s, OMe) 3.37 (2 H, d, OCH_2) 3.72 (6 H, s, CO_2Me) Reqd. (%) Found (%) C, 53.45 53.55 H, 6.8 6.75	δ 1.30—1.73 (2 H, m) 2.32 (1 H, m) 3.52 (2 H, d, CH_2Cl) 3.77 (6 H, s, CO_2Me) Reqd. (%) Found (%) C, 46.5 46.25 H, 5.35 5.4 Cl, 19.15 19.2	δ1.50 (2 H, m) 2.13 (1 H, m) 2.50 (2 H, m, CH_2CN) 3.73 (3 H, s, CO_2Me) 3.78 (3 H, s, CO_2Me) Reqd. (%) Found (%) C, 54.8 54.6 H, 5.6 5.7 N, 7.1 7.4
$:CHPh$	δ 0.02 and 0.08 (each 9 H s), 0.33—2.17 (6 H, m) 6.38—7.58 (5 H, m, Ph) Reqd. (%) Found (%) C, 76.4 76.6 H, 9.85 9.9	δ 0.47—1.77 (12 H, m) 2.04 (1 H, m) 6.78—7.50 (5 H, m, Ph) Reqd. (%) Found (%) C, 89.6 89.3 H, 10.4 10.4	δ 0.65—2.28 (4 H, m) 3.05 and 3.27 (each 3 H, s, OMe) 6.82—7.48 (5 H, m, Ph) Reqd. (%) Found (%) C, 81.45 81.75 H, 8.7 8.7	Not isolated	δ 0.53—2.32 (4 H, m) 2.47 (2 H, m, CH_2CN) 6.75—7.62 (5 H, m, Ph) Reqd. (%) Found (%) C, 84.05 83.75 H 7.05 7.1 N, 8.9 9.05
Cyclopentadienylidene	δ 0.01 (9 H, s, SiMe) 0.80—1.03 (2 H, m) 1.32—2.22 (3 H, m) 5.77—6.53 (4 H, m, C_5H_4) Reqd. (%) Found(%) C, 74.1 74.0 H, 10.15 10.2	δ 0.67—2.25 (12 H, m) 5.85—6.60 (4 H, m, C_5H_4) Reqd. (%) Found (%) C, 89.1 89.1 H, 10.9 10.9	δ 1.35—1.90 (2 H, m) 2.23 (1 H, m) 3.25 (3 H, s, OMe) 3.52 (2 H, d, OCH_2) 5.85—6.60 (4 H, m, C_5H_4 Reqd. (%) Found (%) C, 79.35 79.5 H, 8.9 8.9	δ 1.53—2.08 (2 H, m) 2.48 (1 H, m) 3.33—3.87 (2 H, m) 5.88—6.70 (4 H, m, C_5H_4) Reqd. (%) Found (%) C, 68.35 68.15 H, 6.45 6.5	δ 1.48—2.45 (3 H, m) 2.60 (2 H, m, CH_2CN) 5.83—6.65 (4 H, m, C_5H_4) Reqd. (%) Found (%) C, 82.4 82.6 H, 6.9 6.95 N, 10.7 10.45
Br_2		δ 0.69—2.45 (9 H, m) 3.23—4.43 (3 H, m) Reqd. (%) Found (%) C, 29.55 29.5 H, 4.95 5.0	δ 3.43 (3 H, s, OMe) 3.62—3.92 (4 H, m) 3.92—4.42 (1 H, m) Reqd. (%) Found (%) C, 20.7 20.6 H, 3.5 3.4	δ 3.70—4.12 (4 H, m) 4.37 (1 H, m) Reqd. (%) Found (%) C, 15.25 15.3 H, 2.15 2.1	δ 3.20 (2 H, d, CH_2CN) 3.50—4.05 (2 H, m) 4.05—4.57 (1 H, m) Reqd. (%) Found (%) C, 21.15 21.15 H, 2.2 2.25 N, 6.15 6.15

[a] δ (p.p.m.).

diazomalonate,[15] diazo(phenyl)methane,[16] and diazocyclopentane [17] were prepared by reported methods and identified from spectroscopic data.

Addition Products.—Carbenes were generated and allowed to react with the substrates by the procedure described below; the products were isolated by g.l.c. and characterised by elemental analysis and n.m.r. spectroscopy (Table 3).

Reaction Procedure.—(a) *Reactions of singlet methoxycarbonyl-, bismethoxycarbonyl-, and phenyl-carbenes and cyclopentadienylidene*. A solution of the diazo-compound (0.5 mmol) in a large excess of allylic substrate (20 mmol) in a Pyrex tube immersed in running water maintained at 18 °C was irradiated with a high-pressure mercury lamp (400 W) for 2—3 h.

(b) *Reactions of triplet methoxycarbonyl- and bismethoxycarbonyl-carbenes*.[5] A solution of the diazo-compound (0.5 mmol) and benzophenone (2 mmol) in the allylic substrate (15 mmol) was treated as in (a).

(c) *Bromine addition*. To a stirred solution of the allylic compound (20 mmol) in chloroform maintained at 1 °C (ice-bath) a solution of bromine (0.25 mmol) in chloroform (10 ml) was added during 20 min. The mixture was then stirred for a further 10 min at 1.5 °C.

Competitive Reactions. Competition experiments were carried out on binary mixtures of allylic substrates under thermostatic conditions. Other procedures were the same as above. Yields of the products were determined by use of Ohkura 1700 gas chromatograph equipped with a 2 m Carbowax column. The relative reactivity of two substrates X and Y (k_X/k_Y) was calculated from the equation $k_X/k_Y = P_X/P_Y . I_X/I_Y$, where P_X/P_Y represents relative yields of products from X and Y and I_X/I_Y the molar ratio of X and Y in the initial mixture. The results are summarized in Table 2. Each value of k_X/k_Y is the average of at least three independent runs.

[6/1237 *Received*, 25*th June*, 1976]

---

[15] W. von E. Doering and C. H. De Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955; M. Rosenberger and P. Yates, *Tetrahedron Letters*, 1964, 2285.

[16] D. G. Farnum, *J. Org. Chem.*, 1963, **28**, 870.

[17] T. Weil, *J. Org. Chem.*, 1963, **28**, 2472.