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Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles (8 pages); table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Neighboring Group Participation in Carbene Chemistry. Effect of Neighboring Carboxylate Group on Carbene Reactivities[1]

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Abstract: Reactivities of (alkoxycarbonyl)carbenes are shown to be dramatically changed as one substitutes the ester group with carboxylate group. Thus, (methoxycarbonyl)- or carboxyl(4-nitrophenyl)carbene (**2a** and **2b**, respectively), generated by photolysis of the corresponding diazo compounds in a binary mixture of 2-methyl-2-butene and methanol, gives both cycloaddition products to the butene and OH inserts products into methanol, the relative reactivities ($k_{\mathrm{OH}}/k_{\mathrm{add}}$) being 0.3–0.5. In marked contrast, the "carboxylate" carbene (**2c**) generated from the sodium salt of the diazoacetate under the same conditions produces mostly the OH insertion product at the expense of the cyclopropanes, $k_{\mathrm{OH}}/k_{\mathrm{add}}$ being > 100. The marked effect of the carboxylate group is nicely explained in terms of the participation by the neighboring carboxylate group, which interacts strongly with the vacant p orbital of the singlet carbene, resulting in the reduction of the electrophilicity. The competition experiments using two sets of alkenes with different electron density also support the above idea. Thus, **2c** is > 2000 times more reactive to α-chloroacrylonitrile relative to 1-hexene while **2a** is only 3–4 times more reactive. More intriguingly, a Hammett treatment of the addition of **2** to a series of substituted styrenes demonstrates that philicity of the carbene is converted from electrophilic to nucleophilic in going from **2a** to **2c**. The geometries of the singlet state of the parent carboxylate carbene optimized by the ab initio molecular orbital using the STO-3G basis set is very much like that of α-lactone anion, where strong interaction between carboxylate oxygen anion and the vacant p orbital is possible. ESR studies show, however, that both **2a** and **2c** have a triplet ground state with comparable thermal stability and that the geometry of the triplet state is not affected by the neighboring carboxylate group.

What is the most dramatic and therefore impressive effect of substituents in organic reactions is neighboring group participation[2-4] where the intramolecular association of one group in a molecule exerts a dramatic effect on the reaction course of the other. Thus, in the nucleophilic displacement (S_N) reaction, the reactions proceed particularly rapidly and/or with retained stereochemistry when the nucleophile and the leaving group are in the same molecule. In these molecules, internal nucleophiles become bonded (fully or partially) to the electron-deficient center for an interval of time during the reaction's progress. For example, *o*-(chloromethylsulfonyl)benzoate undergoes hydrolysis quite easily under the conditions where its para isomer is completely inert,[5] and the hydrolysis of α-bromoacetic acids proceeds with retention of configuration of the α-carbon.[6] These results are nicely explained in terms of intramolecular displacement leading to lactones which subsequently undergo attack by the solvent nucleophiles. Such intramolecular displacement, which has been termed anchimeric assistance or neighboring group participation, occurs not only in appropriate organic systems but also in many biological processes.

In carbene chemistry,[7,8] although substituent effects have sustained a high level of attention over the past 15 years, the effect of substituents which are directly bound to, or conjugated with the carbene center has been of primary interest, and no study of such magnitude has been made for the effect of substituents which are insulated from direct conjugation with the carbenic atom. Moreover, the effect of neighboring groups on the reactivity of carbene[9] has been much less dramatic than that in carbenium ion chemistry. This is apparently because carbenes are usually much less electrophilic than carbenium ions. Another reason which should be pointed out here may be that the internal nucleophiles which have been used in carbene reactions are heavily weighted with neutral heteroatom substituents, e.g., ether, carbonyl and halogens.[9]

It is rather surprising to note here that little is known about the effect of neighboring anionic groups such as carboxylate, phosphonate, or sulfonate anions, all of which have been known to act as the most effective participants in the nucleophilic dis-

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† Mie University.

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(2) Lambert, J. B.; Mark, H. W.; Holcomb, A. G.; Magyar, E. S. *Acc. Chem. Res.* **1979**, *12*, 317.

(3) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1.

(4) Brown, H. C. *The Nonclassical Ion Problem*; Plenum: New York, 1977.

(5) Bordwell, F. G.; Cooper, G. D. *J. Am. Chem. Soc.* **1957**, *79*, 916.

(6) Winstein, S.; Hanson, C.; Grunwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 812.

(7) (a) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4.

(8) *Recent Advances in Carbene Chemistry*; Platz, M. S., Ed.; Tetrahedron Symposium in Print 19 1985.

(9) For review, see: Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751.

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Table I. Photolysis[a] of (4-Nitrophenyl)diazoacetate (**1**) in a Binary Mixture (1:3.5) of Methanol-2-Methyl-2-butene

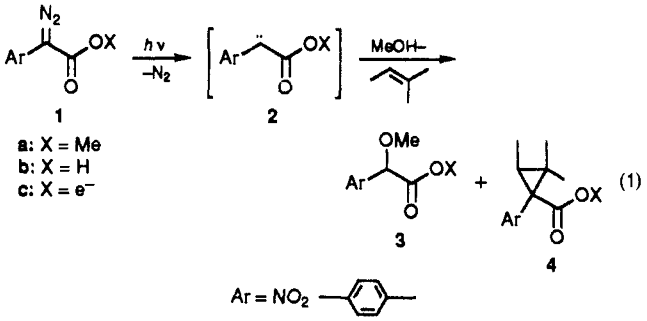
diazo ester (X)	yield,[b] %	
	3	**4** (syn:anti)[c]
1a (Me)	9.2	90.8 (1:0.89)
1b (H)	12.3	87.7 (1:1.2)
1c (e^-)[d]	96.4	3.6 (1:0.50)
1c (e^-)[e]	>99.9	<0.1 (–)

[a] Irradiations were carried out on 5 mL of degassed solutions with 300-W high-pressure mercury arc equipped with a Corning CS-052 filter. [b] Determined by GC on the basis of **1** used. [c] Stereoselectivity of cyclopropanation, syn-aryl/dimethyl. [d] Diazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine. [e] Sodium diazoacetate (**1c**) was used.

placement reaction.[3] One would easily expect that such anionic groups should exert a much more dramatic effect even upon the reactivities of the electrically neutral six electron companion, carbene. In this expectation, we have examined the chemistry of carbenes generated photochemically from diazo carboxylic acid derivatives.

Results and Discussion

Product Analysis Studies. Insertion–Addition Selectivity. Irradiation of methyl (p-nitrophenyl)diazoacetate (**1a**) in a 1:3.5 binary mixture of methanol and 2-methyl-2-butene afforded α-methoxyacetate **3a** and cyclopropanes **4a** (as a mixture of syn and anti isomers) in 7% and 71% yields, respectively. These products are apparently derived from photolytically generated carbene **2a**, which either underwent insertion into the OH bond of methanol or added to the double bond of the alkene. Similar irradiation of the corresponding free diazo acid **1b**, followed by CH_2N_2 treatment gave essentially the same product mixtures. When the sodium salt of **1b** was irradiated under the same conditions, followed by neutralization and esterification, however, the formation of the cyclopropane was almost completely eliminated and α-methoxyacetate **3a** became the major product isolated. Similar irradiation of **1b** in the presence of 2 mol excess of triethylamine also resulted in the almost exclusive formation of the OH insertion product (Table I). It is quite probable that the "carboxylate" carbene **2c** must be generated under these conditions since either the sodium diazoacetate or the amine salt of diazoacetic acid was quantitatively recovered unchanged in the dark under the otherwise same conditions.

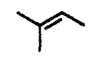
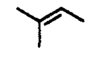


OH insertion–addition selectivities (k_{ins}/k_{add}) were calculated by means of the well-established equation of Doering and Henderson[10]

$$k_{rel} = \frac{k_{ins}}{k_{add}} = \frac{P_i I_a}{P_a I_i} \tag{2}$$

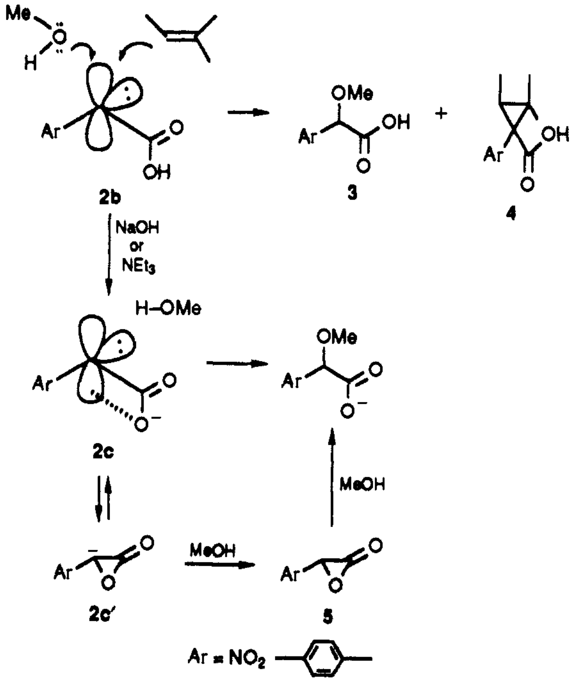
where P_i and P_a are the moles of the OH insertion product and the cyclopropanes and I_i and I_a are the initial moles of methanol and the butene, respectively. The data are listed in Table II. Included in the table for comparison are insertion–addition selectivities of the carbenes having various neutral ester residues X (**2d–h**). It is evident from the data in the table that the neighboring carboxylate group exerts a tremendous effect on the relative reactivities of carbene **2**. Thus, the carbene derived from **1c** is shown to be some 300 times more reactive toward methanol, relative to alkene, than those derived from the diazo ester (**1a**,**d–h**) and the diazo acid (**1b**). A similar dramatic effect of the carboxylate group was observed in the competition reaction using benzene instead of the butene and ethyl mercaptan instead of methanol (Table II).

Table II. Effects of Carboxylate Groups on the Insertion–Addition Selectivities of Carbenes (**2**)[a]

diazo ester (X)	substrates		relative reactivity:
	A	B	k_A/k_B[b]
1a (Me)	MeOH		0.34
1b (H)			0.48
1c (e^-)[c]			>100
1d ($^nC_6H_{13}$)			0.37
1e (^tBu)			0.35
1f (CH_2CF_3)			0.21
1g (CH_2CN)			0.30
1h (CH_2CH_2CN)			0.20
1a (Me)	MeOH	PhH[d]	13
1c (e^-)[c]			>1000
1a (Me)	EtSH[e]		5.1
1c (e^-)[c]			>100

[a] Carbenes were generated in a binary mixture of two substrates A and B. [b] Calculated from the mole fraction of products and substrates. [c] Diazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine. [d] Norcaradienes were formed. [e] SH insertion product was formed.

Scheme I



The difference in the reactivity caused by the carboxylate group is obviously too great to be attributable to a difference in inductive, conjugative, or steric effects, but can be better explained in terms of the neighboring group participation. It is well documented in S_N reactions that the carboxylate group functions as a neighboring group participating in the reaction while the carboxy and ester groups lose a great deal of their effectiveness as a participants.[3] It is quite reasonable, then, to assume that the neighboring carboxylate group can also interact with the vacant p orbital of a singlet carbene. Such interaction should greatly reduce the electrophilicity of the carbene toward external reagents by filling its vacant p orbital. (Methoxycarbonyl)arylcarbenes (**2a**) which we used in this study should be classified as typically electrophilic

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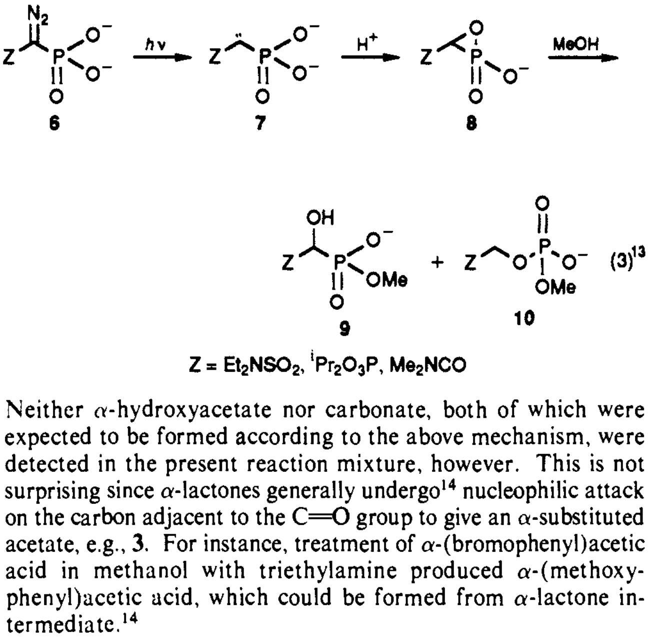
[10] Doering, W. von E.; Henderson, W. A. *J. Am. Chem. Soc.* **1958**, *80*, 5274.

carbenes and therefore react by accepting electrons from the external substrates, e.g., methanol and butenes, into the empty p orbital. Once a carboxylate group is introduced, the vacant p orbital interacts effectively with the internal carboxylate oxygen anion as depicted by **2c** in Scheme I and therefore is no longer available to the external reagents. In other words, the carbenes tend to behave as nucleophiles via the carbenic lone pair rather than as electrophiles. Simple alkenes such as 2-butene are efficient trapping agents for many electrophilic carbenes, but not always reactive toward nucleophilic carbenes.[11] On the other hand, methanol is known to be very reactive to both electrophilic and nucleophilic carbenes, since the former carbene can attack the lone pair electron of oxygen while the latter undergoes protonation.[12] Thus, the carboxylate carbene (e.g., **2c**) showed enhanced reactivity toward alcohol relative to the alkenes (Scheme I).

It may be possible that carbene **2c** can be covalently bonded to the internal carboxylate group leading to the formation of an α-lactone anion **2c′** which then undergoes protonation to give α-lactone **5**.[12a] Subsequent nucleophilic cleavage of **5** by a nucleophile, e.g., methanol, affords the formal OH insertion product. It is quite interesting to note here in this connection that phosphonylcarbene **7** generated from α-diazophosphonate dianions **6** in methanol actually undergoes intramolecular cyclization leading to oxaphosphirane intermediate **8**. Subsequent nucleophilic attack on phosphorus atoms by methanol is followed either by phosphorus–oxygen cleavage to give α-hydroxyphosphonate **9** or by phosphorus–carbon cleavage leading to phosphate **10** (eq 3).[13]



(3)[13]

Z = Et_2NSO_2, ${}^{i}Pr_2O_3P$, Me_2NCO

Neither α-hydroxyacetate nor carbonate, both of which were expected to be formed according to the above mechanism, were detected in the present reaction mixture, however. This is not surprising since α-lactones generally undergo[14] nucleophilic attack on the carbon adjacent to the C=O group to give an α-substituted acetate, e.g., **3**. For instance, treatment of α-(bromophenyl)acetic acid in methanol with triethylamine produced α-(methoxyphenyl)acetic acid, which could be formed from α-lactone intermediate.[14]

It has been reported[14] that α-lactones tend to polymerize in the absence of efficient trapping agents to afford polyesters, which undergo alcoholysis upon heating in alcohol to give α-alkoxy acid. So we irradiated the amine salt of diazo acid (**1b**) in anhydrous benzene which does not react either with carboxylate carbene **2c** nor with α-lactone **5**. No trace of α-methoxy acid **3c** was formed, however, when the photolysis mixtures were refluxed with methanol. The only volatile products detected were *p*-nitrobenzoic acid (5.9%) and *p*-nitrobenzaldehyde (4.2%), both of which were presumably derived by oxidative cleavage of the carboxylate-participating carbene. Since the intermediates generated by irradiation of the neutral diazo compound (**1a** and **b**) were much less susceptible to the oxidation under similar conditions, the formation of these oxidative products can be interpreted as indicating the anionic nature of the intermediate involved in the photolysis of **1c**. Although the results can not afford clear evidence for the presence of α-lactone, its intervention cannot be rigorously excluded. However, the results cannot tell us whether the carboxylate-participating carbene contains a full or partial bond between the divalent carbon and carboxylate oxygen. In order to obtain more insight into the nature of the intermediate, the following labeling experiments were done.

Scheme II

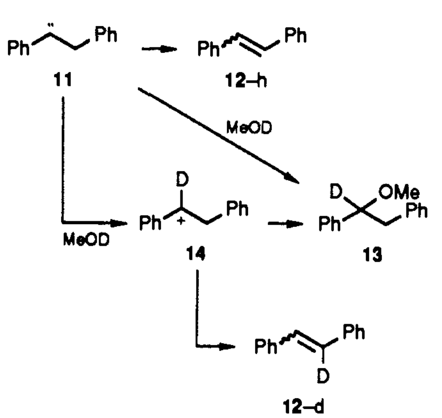


Table III. Photolysis[a] of Sodium 2-Tosylhydrazonate **15** in MeOD

	yield,[b] % (D incorp,[c] %)		
15 (X)	*E*-**17**	*Z*-**17**	**18**
a (Me)	48.1 (<0.1)	42.5 (<0.1)	1.4 (~100)
b (e⁻)	6.6 (28.9)	7.4 (1)	27.9 (~100)

[a] See footnote a to Table I. [b] Determined by GC on the basis of **15** used. [c] Determined by GC-MS.

Mechanism of OH Insertion. Recently we have shown[15] that the philicity of carbene toward alcohols can be roughly judged from deuterium incorporation in the alkene. Carbenes with readily accessible 1,2-hydrogen migration channels incorporated deuterium into the alkene in the presence of MeOD. Thus, 1,2-diphenylethylidene (**11**) generated in MeOD afforded *E*- and *Z*-stilbenes (**12**) in which deuterium was incorporated, along with 1-deuterio-1,2-diphenylethyl methyl ether (**13**). The results can be interpreted as indicating that the phenylcarbenes (**11**) generated in alcohol either undergo 1,2-H migration to yield the stilbenes (**12-h**) or are protonated[16] by the alcohol to give carbocation **14**, which subsequently eliminates a proton and produces the alkene or undergoes nucleophilic trapping by the alcohol to produce the ether (Scheme II). The findings do not indicate that all the ethers are formed via protonation of the carbene. More probably it implies that some of the carbenes should undergo electrophilic attack on the oxygen lone pair of the electron since the phenylcarbenes, e.g., **11**, are recognized to be typical electrophiles. However, it should be noted that the extent of incorporation into the alkene should reflect the philicity of carbenes toward alcohol. Thus, we examined the effect of the neighboring carboxylic groups on the extent of deuterium incorporation in alkene formed from 1-carboxyl-2-phenylethylidene (**16b**) in MeOD in order to get more evidence for the proposed change in the mechanism for OH insertion as it goes from **2a**,**b** to **2c**. The results are summarized

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(11) (a) Richter, R.; Ulrich, H. *J. Org. Chem.* **1971**, *36*, 2005. (b) Brown, J. M.; Place, B. D. *Chem. Commun.* **1971**, 533. (c) Quast, H.; Hunig, S. *Chem. Ber.* **1966**, *99*, 2017. (d) Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.

(12) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935 and references cited therein. (a) A referee has suggested that α-lactone can be formed directly from an excited diazo acetate (**1c**) via cyclization followed by N_2 elimination. This possibility was not eliminated since we were not able to prepare a non-diazo precursor which generated both ester and carboxylate carbenes at presents.

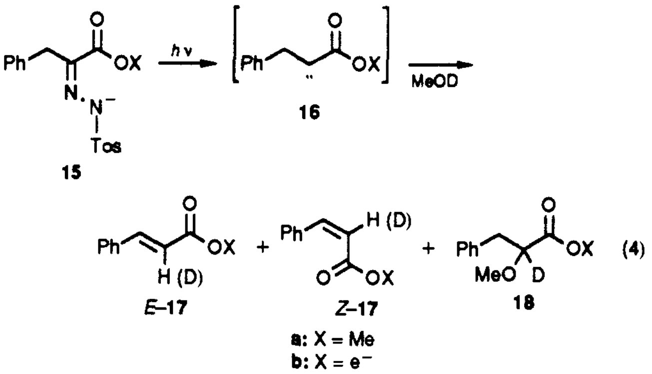
(13) (a) Bartlett, A.; Carruthers, N. I.; Winter, B. M.; Long, K. P. *J. Org. Chem.* **1982**, *47*, 1284. (b) Bartlett, A.; Carruthers, N. I. *J. Chem. Soc., Chem. Commun.* **1982**, 536.

(14) Wheland, R.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6057. Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktaschel, R. *J. Am. Chem. Soc.* **1972**, *94*, 1365. Crandal, J. K.; Sojka, S. A. *Tetrahedron Lett.* **1972**, 1641.

(15) Tomioka, H.; Hayashi, N.; Sugiura, T.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1364.

(16) Friedlich, K.; Jansen, U.; Kirmse, W. *Tetrahedron Lett.* **1985**, *25*, 1936.

in Table III which includes the corresponding ester carbene **16a** for comparison purposes. Intriguing effects of carboxylate anions were observed not only in the percentage of deuterium incorporation but also in product distributions. Thus, the ester carbene **16a** derived from **15a** afforded the alkenes (**17**) almost exclusively as a result of 1,2-H migration (eq 4). This is in accord with the general observation[17] that the singlet carbenes with readily accessible intramolecular reaction channels are not efficiently trapped by external reagents. Once the carboxylate group is introduced, however, the carbene **16b** becomes relatively efficiently trapped by methanol, giving α-methoxybenzylacetate (**18**) at the expense of the alkenes (**17**). This is again explained in terms of the neighboring carboxylate group participation by which the electrophilicity of the carbene is greatly reduced. The mechanism[18] of the 1,2-H shift involves an electrophilic pull of hydride through the vacant p orbital of the singlet carbene. Thus, the decrease in the 1,2-H shift again reflects the reduction of electrophilicity, most probably as a result of the neighboring carboxylate group participation. The extent of deuterium incorporation into **17** is markedly increased as one changes the neighboring group from ester to carboxylate anion, as was to be expected. The deuterated alkenes apparently arise from a carbocation ($PhCH_2C^+HCO_2^-$, **19**) which should be formed by protonation of carbene **16b** or α-lactone anion derived from **16b**, or both. Thus, the above results provide evidence to support the idea that the carboxylate-participating carbenes should undergo protonation by methanol at least more extensively than the ester carbene. The dominant formation of the unlabeled alkenes (**17**) in the MeOD run indicates that not all the carboxylate carbenes (**16b**) react in the participated forms at least in this carbene system. In other words, some of them undergo 1,2-H migration before they are affected by the neighboring carboxylate group.



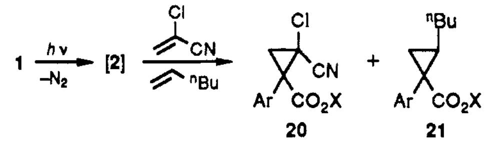
Selectivity in Cyclopropanation. The electrophilic and nucleophilic character of carbenes are not absolute. Any carbene can show both electrophilic and nucleophilic characteristics depending on the nature of reagents with which the carbene reacts. Carbenic philicity[19] has been relatively well characterized on the basis of reactivities toward electron-rich and electron-poor alkenes. Thus, it is of immediate importance to know how the philicity is affected by the neighboring carboxylate participation as based on cyclopropanation selectivity.

Since the carboxylate-participating carbene showed little tendency to react with simple alkenes such as 2-methyl-2-butene, we examined its reactivity toward an electron-deficient alkene, e.g., acrylonitrile. Although conceptually simple, such studies using diazo compounds as precursors for carbene are complicated by the thermal 1,3-dipolar cycloaddition of the diazomethane, especially to electron-poor alkenes, which give pyrazoline that spontaneously decomposes into cyclopropane.[20] Fortunately, however, the diazo ester as well as the acid salt **1** were found to be relatively unreactive toward these alkenes. For example, when the diazo compound and chloroacrylonitrile were allowed to stand for 2 h at 50 °C, only a small amount (<5%) of the expected cyclopropanes (**20**) were formed.[21] Irradiation of the diazo compounds in a binary mixture of 1-hexene and the acrylonitrile were thus carried out at −10 °C for 0.5 h, where the thermal route to cyclopropanes was negligible. The selectivities determined from the product and substrate ratio by using eq 2 for the carbenes of carboxylic acid derivatives are listed in Table IV, which clearly indicates that the philicity was dramatically changed as the ester group was converted to a carboxylate anion group. Thus, the carboxylate-participating carbene is shown to be essentially unreactive toward simple alkenes such as hexene, as has been observed for other typical nucleophilic carbenes, e.g., dimethoxycarbene[22] and (dimethylamino)methoxycarbene.[23]

Table IV. Effects of Carboxylate Groups on the Selectivity in Cyclopropanation[a]

diazo ester (X)	yield,[b] %		k_a/k_b[c]
	20	**21**	
1a (Me)	54.9	43.2	3.51
1b (H)	42.9	48.3	2.48
1c (e^-)[d]	78.9	<0.1	>2000

[a] See footnote a to Table I. [b] Determined by GC. [c] $k_{chloroacrylonitrile}/k_{1\text{-hexene}}$ calculated from the mole fraction of products and substrates. [d] Diazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine.



Hammett Studies. The philicity of carbenes has been examined more quantitatively and generally by a Hammett treatment of the addition of carbene to a series of substituted styrenes. Thus, to date, a variety of carbenes[24] has been classified according to the Hammett ρ values estimated from the addition of carbenes to styrenes and therefore a philicity spectrum among some typical carbenes can be easily obtained. It is desirable then, to know more quantitatively the extent of nucleophilicity caused by the neighboring carboxylate group. More importantly, a Hammett treatment would be expected to provide evidence that philicity

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(17) Baron, W. J.; Decamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. in ref 7(a) Vol. 1, p 20.

(18) (a) Yamamoto, Y.; Moritani, I. *Tetrahedron* **1970**, *26*, 1235. (b) Nickon, A.; Huang, F.-C.; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264. (c) Kyba, E. P.; John, A. M. *Ibid.* **1977**, *99*, 8329. (d) Press, L. S.; Shechter, H. *Ibid.* **1979**, *101*, 509. (e) Su, D. T. T.; Thornton, E. R. *Ibid.* **1978**, *100*, 1872. (f) Dellacoletta, B. A.; Shechter, H. *Tetrahedron Lett.* **1979**, 4817.

(19) For reviews, see: Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58; **1989**, *22*, 15.

(20) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; p 824.

(21) A referee has suggested that pyrazoline formation and subsequent decomposition could be very fast from an excited diazo compound. See also ref 12a.

(22) (a) Hoffmann, R. W.; Lillienblum, W.; Dittrich, B. *Chem. Ber.* **1974**, *107*, 3395. (b) Hoffmann, R. W.; Reiffen, M. *Ibid.* **1976**, *109*, 2565.

(23) Reiffen, M.; Hoffmann, R. W. *Chem. Ber.* **1977**, *110*, 37.

(24) For representative carbene selectivities toward styrenes, see: (a) EtO_2CCH ($\rho = 0.38$); Baldwin, J. E.; Smith, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 1886. (b) CCl_2 ($\rho = -0.62$ at 80 °C); Seyferth, D.; Mui, J. Y. P.; Damraner, R. *Ibid.* **1968**, *90*, 6182. ($\rho = -0.378$ at 0 °C); Sadler, I. H. *J. Chem. Soc.* (*B*) **1969**, 1024. (c) CF_2 ($\rho = -0.57$); Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* **1975**, *97*, 344. (d) $(CH_3)_2C{=}C$ ($\rho = -0.75$); Stang, P. J.; Mangum, M. G. *Ibid.* **1975**, *91*, 6478. (e) $(CH_3)_2C{=}C{=}C$ ($\rho = -0.95$); Patrick, T. B.; Haynie, E. C.; Probst, W. J. *J. Org. Chem.* **1972**, *37*, 1553. (f) Cyclopentadienylidene ($\rho = -0.76$); Dürr, H.; Wendorff, F. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 483. (g) Cycloheptatrienylidene ($\rho = +1.05$); Christensen, L. W.; Waali, E. E.; Jones, W. M. *J. Am. Chem. Soc.* **1972**, *94*, 2118. Duell, B. L.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4901. (h) Benzocyclobutenylidene ($\rho = 1.57$); Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, M., Jr. *Ibid.* **1980**, *45*, 973. (i) Bicyclo[3,2,1]octa-2,6-dien-4-ylidene ($\rho = +0.25$) and Bicyclo[3,2,1]oct-2-en-4-ylidene ($\rho = +0.68$); Murahashi, S.-I.; Okumura, K.; Naota, T.; Nagase, S. *J. Am. Chem. Soc.* **1982**, *104*, 2466. (j) 9-Xanthylidene (ambiphilic); Jones, G. W.; Chang, K. T.; Munjal, R. C.; Shechter, H. *Ibid.* **1978**, *100*, 2922. (k) Ph_2C (ambiphilic); Tomioka, H.; Ohno, K.; Izawa, Y.; Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1984**, *25*, 5415. (l) MeOCCl (ambiphilic); Moss, R. A.; Guo, W.; Krogh-Jespersen, K. *Ibid.* **1982**, *23*, 15. (m) PhOCCl (ambiphilic); Moss, R. A.; Perez, L. A. *Ibid.* **1983**, *24*, 2719.

Table V. Relative Rate Constants for the Addition of the Carbenes (**2a** and **2c**) to Substituted Styrenes (**22**)

Y in $YC_6H_4CH{=}CH_2$ (**22**)	k_Y/k_H[a]	
	2a (X = Me)	**2c** (X = e^-)[b]
4-CH_3	1.46	0.98
H	1.00	1.00
4-Cl	0.61	1.11
4-Br	0.61	1.07
m-Cl	0.62	1.13
p-CN	0.25	2.27

[a] Average of two GC Determinations. [b] Diazo acid (**1b**) was irradiated in the presence of 5 mol excess of triethylamine.

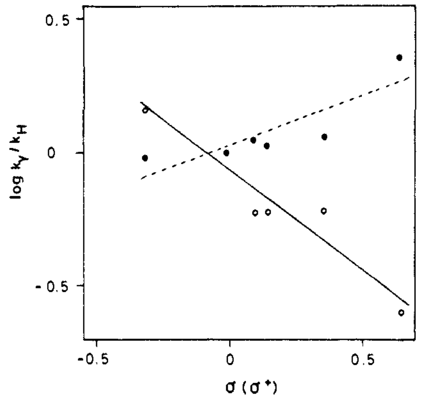
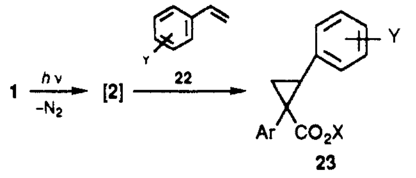


Figure 1. Plot of log k_{rel} vs σ values for the reactions of carbenes **2a** (—) and **2c** (- - -) with substituted styrenes.

of the carbene can be converted from electrophilic to nucleophilic by changing the carbenic substituent from an ester group to an acid anion. Fortunately, the carboxylate-participating carbene adds to a series of substituted styrenes (**22**) to give cyclopropanes (**23**) and hence the Hammett study was possible. The relative reactivities were determined by a competition method in which two styrenes were allowed to compete for a limited amount of the carbene. In a typical run, the precursor diazo compounds were irradiated with a high-pressure mercury lamp through a Corning CS-052 filter (>350 nm) at -10 °C for 0.5 h. In this run, the ratio of styrene mixed with benzene to the diazo compound was more than 20 to 1. Control experiments again showed that the 1,3 dipolar addition of the diazo compounds was negligibly small (<5%) under these conditions.[21a] The relative reactivities of the styrenes were then calculated by the conventional equation[10] (eq 2). The reactions were carried out in duplicate and the results are presented in Table V, along with the data for the ester carbene **2a**.



(6)

Inspection of the results in Table V indicates immediately that the ester carbene **2a** undergoes electrophilic cycloaddition while attacking **22** at the C═C bond, whereas the participating carbene undergoes nucleophilic cycloaddition at that bond. The relative rate constants were then correlated with σ parameters according to Hammett. The ρ values of these Hammett plots (Figure 1) were calculated by a least-squares analysis to be $\rho = -0.75$ ($r = 0.954$) for the ester carbene and $\rho = +0.35$ ($r = 0.834$) for the participating carbene. Thus, the present results clearly indicate that the electrophilic ester carbene is converted to nucleophilic by simply substituting ester residue with hydroxide.

To date, some carbenes have been classified as nucleophiles[24g-i] by the Hammett criterion, although pyrazoline intermediacy is not always rigorously excluded. In this sense, the present positive ρ value of +0.35 for **2c** provides a clear quantitative demonstration of the nucleophilicity of carbene affected by the neighboring carboxylate group. On the other hand, it is not clear whether only the singlet state of the carbene is responsible for the observed positive ρ value since styrenes are known[25,26] to be efficient scavengers for triplet species. However, Hammett studies of addition of triplet carbenes, i.e., 9-xanthylidene[24j] and diphenylcarbene,[24k] to styrenes have revealed that triplet arylcarbenes add to styrenes as ambiphiles. The ambiphilicity can be reasonably attributed to electron-donating or electron-withdrawing substituent stabilization of the benzylic radical center in the triplet 1,3-diradical, which is an obligatory intermediate in the triplet carbene addition.[24k] This rationalization is in accord with indications that benzylic radicals[27] and benzylic 1,3-diradicals[28] can be stabilized by either electron-donating or electron-withdrawing substituents. The linear Hammett relationship even with electron-donating groups observed in the present study suggests that the triplet state would not be involved as a major intermediate and that the singlet state which is able to be affected effectively by the participating carboxylate group (vide infra) is responsible for the observed positive ρ value.

It is quite interesting to compare the ρ value of carbene **2c** with those of carbenes which have been classified[24g-i] as nucleophiles by Hammett studies. Cycloheptatrienylidene[24g] showed the largest positive ρ value of +1.05 among the carbenes studied and therefore is now known as the most nucleophilic carbene in the spectrum of Hammett ρ values. Obviously, the nucleophilicity of cycloheptatrienylidene is believed to be caused by incorporation of the vacant p orbital into an aromatic system. The comparison of these ρ values suggests that the nucleophilicity of **2c** is considerably less than that of cycloheptatrienylidene. This means that the overlap between the vacant p orbital and the neighboring carboxylate group in **2c** is less efficient than that of the incorporation of the vacant p orbital into the aromatic system in cycloheptatrienylidene. Apparently, the participation in **2c** would require the formation of a strained, three-membered ring, reducing the effectiveness of the neighboring group participation.

Detection of Triplet Carbenes by ESR Spectroscopy. Almost all arylcarbenes are known to be triplets in their ground states.[29] However, if the perturbation of the electronic structures of the carbene by the neighboring carboxylate group is large enough, it will be possible for the ground state of the carbene **2c** to be a singlet. Thus, in order to assign the ground state for the carbenes and investigate the structures of their triplet states, we tried to measure the ESR spectrum of the carbenes **2**.

Irradiation of methyl (*p*-nitrophenyl)diazoacetate (**1a**) in a rigid glass of ethanol at 15 K in an ESR cavity with Pyrex-filtered UV light produced signals in the range from 140 mT to 820 mT in the X-band ESR spectrum (microwave frequency = 9.296 GHz). The intense signal at 332.7 mT is assigned to doublet radicals presumably formed from chemical reactions of the carbene with matrices. The signals at 147.3, 441.7, 594.7, and 815.2 mT are assigned to Hz, Hx, Hy, and Hz transitions of a triplet, respectively. The weak but significant signals detected at 465.2 and 576.0 mT show the presence of a minute quantity of another triplet species. Two Hz transitions of the minor triplet species are thought to overlap with those of the major species. The zero-field splitting (zfs) parameters are calculated to be $D = 0.4530$ cm^{-1} and $E = 0.0377$ cm^{-1} for the major species, and $D = 0.4521$ cm^{-1} and $E = 0.0274$ cm^{-1} for the minor species, respectively. It is quite reasonable that these triplet species are regarded as triplet carbenes in their triplet states, because their zfs parameters are in the range of the values reported on various arylcarbenes.[29] Thus it is concluded that the irradiation of **1a** in a rigid glass produces two

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(25) Gaspar, P. P. in ref 7a Vol. 2. Chapter 6.

(26) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4015.

(27) Dinçtürk, S.; Jackson, R. A.; Townson, M.; Agirbas, H.; Billingham, N. C.; March, G. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1121. Dinçtürk, S.; Jackson, R. A. *Ibid.* **1981**, 1127. Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.

(28) Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlak, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5896.

(29) Trozzolo, A. M.; Wasserman, E. In ref 7a Vol. 2, pp 189-199.

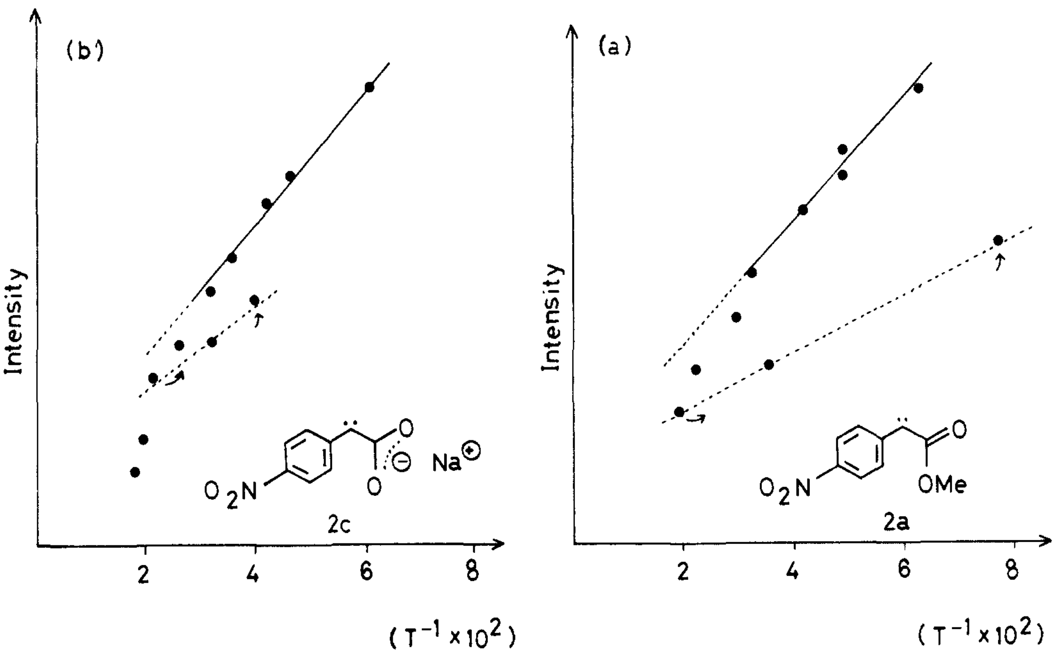
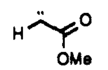
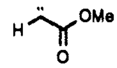


Figure 2. Curie plots of triplet signals after the photolysis of **1a** (a) and **1c** (b). Arrow and dotted lines indicate reproduction of the intensity of triplet signals upon lowering the temperature after warming up to ca. 50 K.

Table VI. Assignment of the Zero-Field Splitting Parameters to the Geometric Isomers of **24**[a]

carbenes (**24**)		D, cm^{-1}	E, cm^{-1}	E/D
	(trans)[b]	0.617	0.053	0.086
	(cis)	0.663	0.030	0.045

[a] Reference 30. [b] The major isomer.

isomeric triplet carbenes which are distinguished by their E values.

In contrast, the spectra recorded after the irradiation of sodium (p-nitrophenyl)diazoacetate (**1c**) contained a series of signals due to a single triplet carbene together with an intense doublet signal. It is noted that the resonance positions of the carbene differ from those of the major species generated by the irradiation of the ester **1a** and they are rather close to those of the minor one. The zfs parameters of the carbene in the triplet state are calculated to be $D = 0.4572$ cm^{-1} and $E = 0.0271$ cm^{-1}.

Comparing the D values observed for the carbene **2a** with that reported for (p-nitrophenyl)carbene ($D = 0.4859$ cm^{-1}),[29] it is indicated that the distance between the two unpaired electrons is longer in **2a** than in (p-nitrophenyl)carbene. The decrease of the D value in the carbene **2a** is reasonably explained by the delocalization of the π spin onto the carbonyl oxygen.

Hutton and Roth reported that the ESR spectra of carbomethoxycarbene (**24**) showed two sets of triplet signals with slightly different zfs parameters.[30] They assigned the major isomer with the lower D value to the carbene with trans conformation and the minor isomer with the higher D value to the cis isomer, by taking into account the contribution of the spin density on the carbonyl oxygen to the zfs parameters. Their assignment is summarized in Table VI. It is not surprising that the geometric isomerism is also observed for the carbene **2a**, since the π spin in **2a** is expected to be delocalized largely on the carbonyl oxygen as mentioned above. Moreover a large decrease of the E/D value is observed in going from the major to the minor isomer of **2a**. This tendency is in harmony with that reported in the geometric isomers of **24** shown in Table VI. Thus the two isomeric carbenes observed by the irradiation of **1a** are reasonably identified as the geometric isomers of carbene **2a**; the major isomer is assigned to the trans **2a**-t, and the minor is assigned to the cis isomer **2a**-c. The zfs parameters and their assignments are summarized in Table VII.

It should be emphasized again that the zfs parameters of the carboxylate carbene **2c** are different from those of the major isomer **2a**-t and almost identical with those of the minor isomer **2a**-c. There are several possible explanations for this result. First, the conformation of the carboxylate carbene **2c** could be identical with that of the minor isomer of the ester. This possibility seems unlikely, because it is reasonable to think that the two oxygen atoms of the carboxylate anion become equivalent in polar solvents such as ethanol, so that the phenomenon of geometric isomerism is impossible in **2c**. The second possibility is that the angle of the divalent carbon of the carbene **2c** would be quite different from that of **2a**-t. This explanation would be possible if the intramolecular interaction of the carboxylate anion with the carbenic center resulted in structural changes of the triplet carbene in a rigid glass. The E/D value is known to reflect the angle of the divalent carbon; the increase of the angle results in the decrease of the E/D values.[31] However, in the case of the carbenes with unsymmetrical π spin distribution such as carboalkoxycarbenes, the spin distribution plays an important role in the determination of the zfs parameters. Therefore, the smaller E/D value of the carboxylate carbene **2c** does not necessarily indicate the larger angle of the divalent carbon of **2c**. The significant differences between the zfs parameters in the isomeric carbomethoxycarbenes (**24**) have been attributed not to the different spin densities and angles of the divalent carbons, but to the different spin distributions, that is, the different contributions of the π spin density on the carbonyl oxygen to the parameters.[30]

The most probable explanation for the drastic changes of zfs parameters in the carboxylate carbene **2c** is that the contribution of the carbonyl oxygen to the zfs parameters is eliminated in **2c** because of the disappearance of the carbonyl functional group. The zfs parameters of the major isomer of **2a**, which is assigned to the trans isomer **2a**-t, is thought to be predominantly governed by the large spin density on the carbonyl oxygen, as discussed by Hutton and Roth.[30] Since in the cis isomer of **2a** the contribution of the carbonyl oxygen to the zfs parameters is small, the parameters are thought to reflect the spin density and the angle of the divalent carbon atom. The agreement of the zfs parameters of the cis isomer **2a**-c with those of the carboxylate carbene **2c**

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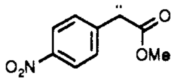
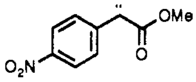
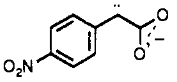
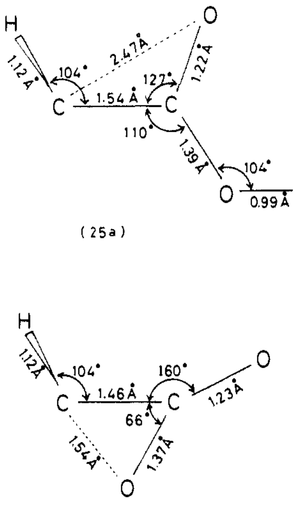
[30] Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324. See also Roth, H. D.; Hutton, R. S. *Tetrahedron* **1985**, *41*, 1567.

[31] Wasserman, E.; Kuck, V. J.; Hutton, R. S.; Yager, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 7491.

Table VII. The Zero-Field Splitting Parameters for Carbenes **2a** and **2c**

carbenes		D, cm^{-1}	E, cm^{-1}	E/D
	(**2a**-t)	0.4530	0.0377	0.0832
	(**2a**-c)	0.4521	0.0274	0.0606
	(**2c**)	0.4572	0.0271	0.0593



(25a)

(25b)

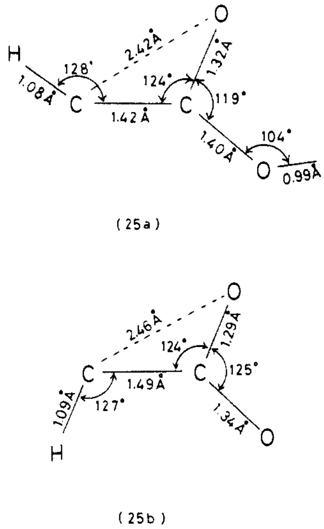
Figure 3. Optimized geometries for the singlet acid carbene $HCCO_2H$ (**25a**) and the singlet carboxylate carbene $HCCO_2^-$ (**25b**). Bond lengths are in angstroms and angles are in degrees.

seems to imply that the contribution of the carboxylate anion to the π spin density at the divalent carbon and to the structure of the carbene is negligible in the triplet state.

The spin multiplicities of the ground state of the carbenes, **2a** and **2c**, were determined from the temperature dependence of the intensities of their ESR signals. The intensities of both carbenes, **2a** and **2c**, decreased linearly with the reciprocal of the temperature in the range of 10–30 K, as shown in Figure 2. The linear relations indicate that both carbenes are likely to have a triplet ground state, though the possibility can not be excluded that the triplet lies ca. 10 cal/mol above the singlet ground state. The plots deviated irreversibly from the line at above 30 K, but linear relations were obtained again by lowering the temperature as indicated by the arrows and the dotted line in the figure. These results are explained by a partial loss of carbenes at the higher temperature, owing to the chemical reactions of the triplet with a matrix or of a more reactive singlet state populated thermally. Thus the thermal stability of the triplet carbene **2c** in a rigid matrix is found to be comparable to that of **2a**.

The ESR studies revealed that the carboxylate carbene **2c** had a triplet ground state. Moreover we have obtained no evidence for the interaction of the carboxylate anion with the carbenic center in the triplet state of **2c**. Thus the results obtained for the triplet state by the ESR spectroscopy present a striking contrast to the reactivities of the singlet state in fluid solutions. This seems to be because the interaction of the vacant p orbital of the carbene in the singlet state with the carboxylate anion moiety is more effective than that of the half-occupied p orbital in the triplet state.

Theoretical Calculations. Ab initio MO calculations offer further corroborating evidence for the neighboring participation of the carboxylate group on carbene chemistry. The geometries of the singlet state of the parent carboxylic acid (**25a**) and the carboxylate carbene (**25b**) optimized by ab initio molecular orbital using the STO-3G basis set are shown in Figure 3. Inspection of the optimized geometries immediately reveals that the geometry changes dramatically in going from acid carbene to anion carbene. Thus, in the carboxylate carbene, the C_1–C_2–O_2 bond angle is expanded up to 160° whereas the C_1–C_2–O_1 bond angle is contracted to 66.0° and consequently the distance between carbenic carbons and oxygen anions is calculated to be 1.54 Å, which is as short as that of a carbon–carbon single bond. The whole geometry of **25b** is then very much like that of an α-lactone anion, suggesting that there should be strong interaction between a carbenic carbon and an oxygen anion, as has been proposed from the product analysis studies. Obviously, no such interaction is expected from the inspection of the geometry of acid carbenes (**25a**).



(25a)

(25b)

Figure 4. Optimized geometries for the triplet acid carbene $HCCO_2H$ (**25a**) and the triplet carboxylate carbene $HCCO_2^-$ (**25b**). Bond lengths are in angstroms and angles are in degrees.

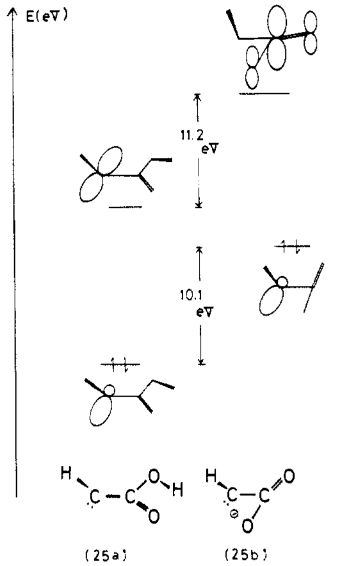


Figure 5. Energies and shapes of the frontier orbitals of singlet **25a** and **25b**.

Optimized geometries of the corresponding triplet carbene were also calculated by using the same basis set and are shown in Figure 4 for comparison purposes. It is immediately clear that no significant change in geometries is seen in going from acid to anion carbenes in the case of the triplet. This is again in accord with the spectroscopic observation that the geometries of the triplet carbene are not significantly affected by the neighboring groups.

Energies of frontier MO also support the idea that the carboxylate carbene is more nucleophilic than acid carbenes (Figure 5). Thus, the energies of HOMO as well as LUMO are greatly raised as the neighboring group is changed from acid to acid anion.

Obviously, such change in the energy predicts that the interaction with the carbene HOMO becomes more favorable than that with the LUMO, as is observed.

Concluding Remarks. The present results demonstrate that typical neighboring groups such as carboxylate groups, which have been known to exert a dramatic effect on nucleophilic displacement, show similar dramatic effects on the fate of carbenes. Impressive changes in the reactivity in going from carboxylic acid to the carboxylate anion group, which have been well documented in the solvolysis reaction, are also shown to exist in the carbenic reactions. Such a dramatic effect of substituents have not been precedented in the reaction of carbenes, which are electronically neutral and therefore much less susceptible to the electronic change in substituents.

All of these findings clearly provide concrete evidence that carbenic reactivities are susceptible to a similarly dramatic influence of the participants as that established in electrically positive six electron companions.

Rate enhancement and retained stereochemistry have served as useful tests for the neighboring group participation in the solvolysis reaction. In carbene chemistry, no diagnostic tests for neighboring group participation have been established. Obviously, stereochemical tests which have been used in carbenium chemistry can not be applied to carbene chemistry since carbenes have no stereochemical handle. Here we propose that the relative reactivity changes reflecting rate enhancement can be used as a useful and convenient test for neighboring group participation. Thus, electrophilic to nucleophilic inversion caused by typical participants can be most easily judged by simply examining the OH insertion-cyclopropanation selectivities. Cyclopropanation selectivity determination using a proper set of two electronically different alkenes offers corroborating evidence, and philicity determination using the Hammett treatment of the addition to a series of substituted styrenes enables more quantitative evaluation of the degree of the participation. Those tests can conveniently be used as an equally attractive diagnosis for the neighboring group participation in carbene chemistry.

In spite of the chemical evidence that the reactivities of carbenes are dramatically changed as a result of the strong perturbation by the neighboring carboxylate group, ESR studies provided unequivocal evidence that the ground-state multiplicities are not affected by the neighboring group. It is very important to note here in this connection that the geometrical changes of the molecules are usually very difficult in rigid organic matrices at this low temperature. For example, it has been reported[32] that when a carbene is generated in microscopically rigid glass, it has the best geometry and the conformation dictated by the precursor and undergoes irreversible structural change to the thermodynamically most stable geometry as the media become soft at high temperature. Thus, it is probable that carboxylate carbenes have, from their birth from the diazo precursor at low temperature in rigid glass, the geometry which should reflect the geometry and the conformation of the precursor. Efficient interaction of the carbenic p orbital with the carboxylate group is not attained in the nascent geometry of the carboxylate carbene and a structural movement against steric demand imposed by the highly rigid environments will be required in order to maximize the overlap between the orbitals. Temperature studies of ESR signals showed that the structural change was not attained at least in the triplet manifold. This is presumably due to the ineffective interaction of the half-occupied p orbital with the carboxylate anion moiety. Although the ESR studies give us no information on the geometrical change in the singlet state of carbenes, it is now well documented[33] that the reactions of carbene within rigid organic matrices are strongly affected by that rigidity. Moreover, the ionic nature of the participating carbene (e.g., **2c** or **2c′**) must be strongly favored by the solvation, which is apparently not attained in rigid matrices.

Finally, it is important to consider whether the interaction between the carbene center and a carboxylate group is partial or full. The theoretical calculation on model carbene (**25b**) suggests that the bond length between carbenic carbons and oxygen anions is indistinguishably close from that known for cyclopropane itself, suggesting full bonding that forms an α-lactone anion is possible. It is probable that α-lactone formed by protonation of its anion may intervene in the reaction in protic substrates, e.g., methanol. The intermediates undergoing cyclopropanation to the alkenes, on the other hand, seem to have a carbenic character unlike α-lactone or its anion. Unfortunately, we have no experimental means to make a clear distinction between the carboxylate carbene and α-lactone anion at present. It is very tempting then to assume the carboxylate carbene (**2c**) and the α-lactone anion (**2c′**) are in equilibrium. Apparently, further experimental, as well as theoretical, studies are needed to clarify these points.

Experimental Section

General Methods. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrophotometer, and ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 ev). The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column A was prepared from 10% SE-30 on Diasolid L (5.0 mm × 2.0 m); column B consisted of 5% PEG-20M on Diasolid L (5.0 mm × 1.0 m). Thin-layer chromatography was done on a Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on silica gel (ICN for dry column chromatography).

ESR Measurements. The diazo compounds were dissolved in ethanol (ca. 5×10^{-3} M) and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission ESR cavity at 15 K with an Air Products LTD-3-100 liquid helium transfer system, and irradiated with an Ushio USH-500D 500-W high-pressure mercury lamp and a Pyrex filter. ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a Varian E-500 NMR gaussmeter.

Irradiations for Product Identification. In a typical run, a solution of the diazo compounds (ca. 100 mg) in substrate (5 mL) was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The resulting solution with the diazoacetic acid **1b** and acetate **1c** was treated with diazomethane shortly after the irradiation. The irradiation mixtures were then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS. These fully characterized products were then used as "authentic" compounds for product identification by coinjection in GC-MS.

Irradiations for Analytical Purposes. All irradiations outlined in Tables I–V were carried out in a Pyrex tube of 5.0-mL capacity at below 10 °C. In order to avoid ambiguity of the relative yields due to the oxidation, the solution was degassed by subjecting the samples to a minimum of three freeze–degas–thaw cycles at pressure near 10^{-5} mmHg before irradiation. Irradiation was generally continued until all the diazo compound was destroyed. Product identifications were established either by GC as well as GC-MS Comparisons with authentic samples and product distributions were conveniently determined by standard GC techniques.

General Comments concerning the Competition Experiments. These were carried out on binary mixtures of two substrates under the carefully controlled conditions. Thus, the precursory diazo compounds (0.1 mmol) were dissolved in the solvents (5 mL) consisted from large excess of the two substrates. Generally no solvents were used to avoid possible effect of solvent on the reactivities of carbenes. The reaction mixtures were degassed and irradiated as described above and product ratios were determined on a Yanagimoto gas chromatograph equipped with a calibrated flame ionization detector, coupled to a Shimadzu C-R1B digital electronic integrator. The reaction mixtures with the diazoacetic acid (**1b**) and acetate (**1c**) were treated with diazomethane before the GC analysis. Control experiments exclude the possible photoconversion of the products during the irradiation period and also demonstrate that no reaction occurs in the absence of light. Experiments were duplicated, and average deviations from the mean values were all <3%.

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Table VIII. Physical Data of (4-Nitrophenyl)diazoacetates **1a–h**

1	X in 1	mp, °C	IR, cm^{-1}	NMR, δ
a	Me	147.0–149.0	2090, 1708, 1590	8.16 (2 H, d, *J* = 8.0 Hz), 7.60 (2 H, d, *J* = 8.0 Hz), 3.88 (3 H, s)
b	H	124.3–125.2	2095, 1645	
c	Na	>300	2095, 1612, 1591	
d	$^{n}C_6H_{13}$	53.0–55.8	2105, 1705, 1590	8.15 (2 H, d, *J* = 8.5 Hz), 7.58 (2 H, d, *J* = 8.5 Hz), 4.28 (2 H, t, *J* = 6.0 Hz), 1.80–1.30 (8 H, m), 0.90 (3 H, t, *J* = 6.0 Hz)
e	^{t}Bu	117.0–118.5	2085, 1685, 1590	8.53 (2 H, d, *J* = 8.5 Hz), 7.55 (2 H, d, *J* = 8.5 Hz), 1.56 (9 H, s)
f	CH_2CF_3	76.0–83.0	2120, 1720, 1595	8.17 (2 H, d, *J* = 8.5 Hz), 7.70 (2 H, d, *J* = 8.5 Hz), 4.75 (2 H, q, *J* = 8.0 Hz)
g	CH_2CN	129.3–132.7	2100, 1720, 1590	8.17 (2 H, d, *J* = 8.0 Hz), 7.57 (2 H, d, *J* = 8.0 Hz), 4.89 (2 H, s)
h	CH_2CH_2CN	107.6–110.9	2100, 1705, 1595	8.13 (2 H, d, *J* = 8.5 Hz), 7.55 (2 H, d, *J* = 8.5 Hz), 4.52 (2 H, t, *J* = 6.0 Hz), 2.80 (2 H, t, *J* = 6.0 Hz)

Table IX. NMR and MS Data of α-Methoxy-α-(4-nitrophenyl)acetates **3a,d–h**

	NMR, δ				MS:
3	Ar	ArCH	MeO	other	*m/e* (rel intensity)
a	8.05 (2 H, d, *J* = 8.0 Hz), 7.52 (2 H, d, *J* = 8.0 Hz)	4.78 (1 H, s)	3.45 (3 H, s)	3.70 (3 H, s)	166 (100) 120 (30)
d	8.14 (2 H, d, *J* = 8.0 Hz), 7.55 (2 H, d, *J* = 8.0 Hz)	4.75 (1 H, s)	3.44 (3 H, s)	4.06 (2 H, t, *J* = 6.0 Hz), 1.65–1.18 (8 H, m), 0.94–0.80 (3 H, m)	166 (100) 120 (22)
e	8.14 (2 H, d, *J* = 8.0 Hz), 7.55 (2 H, d, *J* = 8.0 Hz)	4.62 (1 H, s)	3.44 (3 H, s)	1.39 (9 H, s)	166 (100) 120 (32)
f	8.20 (2 H, d, *J* = 8.0 Hz), 7.62 (2 H, d, *J* = 8.0 Hz)	4.98 (1 H, s)	3.49 (3 H, s)	4.50 (2 H, q, *J* = 8.0 Hz)	166 (100) 120 (8)
g	8.20 (2 H, d, *J* = 8.0 Hz), 7.62 (2 H, d, *J* = 8.0 Hz)	4.97 (1 H, s)	3.49 (3 H, s)	4.77 (2 H, s)	166 (100) 120 (29)
h	8.19 (2 H, d, *J* = 8.0 Hz), 7.62 (2 H, d, *J* = 8.0 Hz)	4.92 (1 H, s)	3.47 (s, 3 H)	4.32 (2 H, t, *J* = 6.0 Hz), 2.70 (1 H, t, *J* = 6.0 Hz), 2.67 (1 H, t, *J* = 6.0 Hz)	166 (100) 120 (25)

The runs using alkenes with electron-deficient double bond were carried out at a lower temperature in order to avoid the thermal pyrazoline pathway. Thus, the precursory diazo compounds were added to the substrate mixture precooled to −20 °C and the mixtures were carefully degassed and irradiated at −10 °C. Control experiments exclude the formation of cyclopropanes in the absence of light under these conditions.

Preparation of (4-Nitrophenyl)diazoacetic Acid Derivatives 1a–c. (4-Nitrophenyl)diazoacetic acid (**1b**) was prepared according to the procedure of Schank[34] by diazo group transfer of tetrahydropyranyl (4-nitrophenyl)diazoacetate with tosyl azide followed by the acid-catalyzed hydrolysis of the resulting diazo ester. The sodium salt of the diazoacetic acid was obtained by the treatment of **1b** with NaOMe in absolute ether followed by the filteration and washing with the ether. Both **1b** and **1c** were considerably stable in the dark at 0 °C. All other (4-nitrophenyl)diazoacetates (**1d–h**) were prepared by the diazo group transfer of the corresponding phenylacetate with tosyl azide according to the slightly modified method of Regitz.[35] Typically, to a solution of the ester (10 mmol) and triethylenediamine (20 mmol) in anhydrous acetonitrile (20 mL) was added an acetonitrile solution of tosyl azide (10 mmol) at 0–5 °C under vigorous stirring in the dark. The progress of the reaction was carefully monitored by TLC and after almost all of the starting materials were consumed, the reaction mixture was poured into water (150 mL) to give orange to yellow crystalline of **1**, which was filtered and washed with water and a small amount of cold methanol. The crystalline product dried under reduced pressure (10^{-1} Torr) at room temperature was found to be pure spectroscopically. Spectral data are given in Table VIII.

Preparation and Decomposition of Sodium Salt of 1-Phenyl-2-ketopropionic Acid Tosylhydrazonate (15) in MeOD. 1-Phenyl-2-ketopropionic acid[36] (0.67 g, 4.1 mmol) was dissolved in methanol (20 mL). To this was added an equivalent amount (0.76 g, 4.1 mmol) of (*p*-tolylsulfonyl)hydrazine. The mixture was stirred until the tosylhydrazine dissolved to give a pale yellow solution. After standing for 3 days at room temperature, the precipitate was filtered, washed with cold methanol, and dried under vacuum (1.20 g, 3.6 mmol): yield, 88.1%; mp 170–175 °C; NMR (δ, $CDCl_3$) 7.75 (2 H, d, *J* = 8.0 Hz), 7.60–7.05 (7 H, m), 3.76 (2 H, s), 2.43 (3 H, s).

The acid tosylhydrazone (0.10 g, 0.3 mmol) thus obtained was dissolved in absolute ether (10 mL) and treated with excess of CH_2N_2. Evaporation of the solvent afforded the corresponding methyl ester as an yellow oil in quantitative yield: NMR (δ, $CDCl_3$) 7.77 (2 H, d, *J* = 8.0 Hz), 7.34 (2 H, d, *J* = 8.0 Hz), 7.25 (5 H, br s), 4.25 (2 H, s), 3.74 (3 H, s), 2.43 (3 H, s).

To a suspension of sodium hydride (50 mg of NaH in oil (50%) was washed with dry ether, 0.6 mmol) in dry THF (5 mL) was added tosylhydrazone (0.30 mmol for the acid, 0.6 mmol for the ester). The mixture was stirred for 1 h under argon and the precipitate was filtered, washed with cold dry THF under argon atmosphere and dried in vacuum to afford the sodium salt, which was immediately used for the photolysis experiments.

The sodium salt (3 mg) was dissolved in MeOD (Merck, 99.9%, 0.5 mL) in a Pyrex tube. After careful degassing, the mixture was irradiated as described above. A faint pink color and copious gas evolution was observed during the irradiation, indicating the formation and decomposition of the corresponding diazo compounds. The mixture was irradiated until the color disappeared. The photomixture from **15b** was treated with CH_2N_2. The contents of deuterium in the products (**17** and **18**) were conveniently determined by using standard GCMS technique. In order to avoid the possible error due to partial separation of isotopic mixtures by GC, the mass fragmentgraphy technique was employed. Thus, total ion of each mass (*m/e*) were integrated in each GC peaks and used as numerical value in calculation[37] of analysis.

The OH Insertion Product (3) of 2 to Methanol. A solution of the diazo compounds (**1**, ca. 50 mg) in dry methanol (5 mL) in a Pyrex tube was irradiated by using a Corning CS-052 filter (>350 nm) at 10 °C. After evaporation of the solvent under reduced pressure, the reaction mixture was subjected to silica gel chromatography to afford pure α-methoxy-α-arylacetate (**3**) in about 85–90% yields. NMR and MS data are summarized in Table IX. Anal. (**3e**) Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.87; H, 6.35; N, 5.07.

The Cycloadducts (4) of 2 to 2-Methyl-2-butene. A solution of the diazo compounds (**1**, ca. 50 mg) in the butene (3 mL) in a Pyrex tube was irradiated under the similar condition employed for the photoreaction in methanol. The reaction mixture was separated by preparative TLC ($CHCl_3$–*n*-hexane = 1:1) to give isomerically pure 1,1,2-trimethyl-3-(methoxycarbonyl)-3-(4-nitrophenyl)cyclopropanes. NMR and MS data are given in Table X.

Photolysis of 1a in Benzene. A solution of **1a** (50 mg) in benzene (5.0 mL) was irradiated and the irradiated mixture was separated by preparative TLC ($CHCl_3$–*n*-hexane = 3:1) to give 1-(methoxycarbonyl)-1-(4-nitrophenyl)norcaradiene (45 mg) in 74.0% yield: NMR (δ, CCl_4) 8.00–7.15 (4 H, m), 6.31–5.80 (4 H, m), 4.12–4.08 (2 H, m), 3.60 (3 H, s); MS *m/e* (rel intensity) 271 (M^+, 16), 239 (45), 212 (100), 166 (18). Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 65.65; H, 4.71; N, 4.98.

The SH Insertion Product of 2 in Thioethanol. A solution of **1a** (50 mg) in thioethanol (50 mL) was irradiated and the photomixture was chromatographed to afford α-thioethoxy-α-(4-nitrophenyl)acetate (53 mg) in 91.9% yield: NMR (δ, $CDCl_3$) 8.08 (2 H, d, *J* = 8.5 Hz), 7.55

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Table X. NMR and MS Data of 1,1,2-Trimethyl-3-(methoxycarbonyl)-3-arylcyclopropanes **4a,d–h**

		NMR, δ		MS:
4	(syn/anti)[a]	Ar	other	m/e (rel intensity)
a	(syn)	8.12 (2 H, d, J = 8.0 Hz), 7.32 (2 H, d, J = 8.0 Hz)	3.55 (3 H, s), 1.40–0.80 (10 H, m)	263 (M^+, 20), 248 (35), 231 (40), 216 (25), 115 (38), 73 (100)
	(anti)	8.09 (2 H, d, J = 8.0 Hz), 7.42 (2 H, d, J = 8.0 Hz)	3.54 (3 H, s), 1.38–0.80 (10 H, m)	
d	(syn)	8.14 (2 H, d, J = 8.0 Hz), 7.34 (2 H, d, J = 8.0 Hz)	3.97 (2 H, t, J = 6.0 Hz), 1.99 (1 H, q, J = 7.0 Hz), 1.63–0.82 (20 H, m)	333 (M^+, 7), 249 (100), 234 (41), 163 (55), 59 (47)
	(anti)	8.09 (2 H, d, J = 8.0 Hz), 7.42 (2 H, d, J = 8.0 Hz)	3.96 (2 H, t, J = 6.0 Hz), 1.63–0.80 (21 H, m)	
e	(syn)	8.11 (2 H, d, J = 8.0 Hz), 7.32 (2 H, d, J = 8.0 Hz)	1.88 (1 H, q, J = 7.0 Hz), 1.30 (3 H, s), 1.28 (9 H, s), 0.96 (3 H, d, J = 7.0 Hz), 0.92 (3 H, s)	249 (50), 163 (29), 57 (100)
	(anti)	8.09 (2 H, d, J = 8.0 Hz), 7.43 (2 H, d, J = 8.0 Hz)	1.58 (1 H, q, J = 7.0 Hz), 1.32 (9 H, s), 0.80 (3 H, s)	
f	(syn)	8.12 (2 H, d, J = 8.0 Hz), 7.33 (2 H, d, J = 8.0 Hz)	4.57–4.14 (2 H, m), 2.03 (1 H, q, J = 7.0 Hz), 1.32 (3 H, s), 1.02 (3 H, d, J = 7.0 Hz), 0.98 (3 H, s)	331 (M^+, 41), 231 (59), 216 (36), 141 (100), 115 (41)
	(anti)	8.08 (2 H, d, J = 8.0 Hz), 7.42 (2 H, d, J = 8.0 Hz)	4.33 (2 H, q, J = 8.0 Hz), 1.57 (1 H, q, J = 7.0 Hz), 1.37 (3 H, d, J = 7.0 Hz), 1.32 (3 H, s), 0.84 (3 H, s)	
g	(syn)	8.16 (2 H, d, J = 8.0 Hz), 7.33 (2 H, d, J = 8.0 Hz)	4.76–4.40 (2 H, m), 2.08 (1 H, q, J = 7.0 Hz), 1.36 (3 H, s), 1.02 (3 H, d, J = 7.0 Hz), 0.97 (3 H, s)	288 (M^+, 55), 231 (84), 157 (75), 123 (90), 115 (85), 98 (100), 69 (74)
	(anti)	8.11 (2 H, d, J = 8.0 Hz), 7.42 (2 H, d, J = 8.0 Hz)	4.58 (2 H, s), 1.57 (1 H, q, J = 7.0 Hz), 1.37 (3 H, d, J = 7.0 Hz), 1.33 (3 H, s), 0.84 (3 H, s)	
h	(syn)	8.15 (2 H, d, J = 8.0 Hz), 7.36 (2 H, d, J = 8.0 Hz)	4.37–4.02 (2 H, m), 2.55 (2 H, t, J = 6.0 Hz), 2.04 (1 H, q, J = 7.0 Hz), 1.34 (3 H, s), 1.01 (3 H, d, J = 7.0 Hz), 0.95 (3 H, s)	302 (M^+, 29), 285 (100), 231 (70), 157 (80), 115 (67), 59 (85)
	(anti)	8.11 (2 H, d, J = 8.0 Hz), 7.45 (2 H, d, J = 8.0 Hz)	4.18 (2 H, t, J = 6.0 Hz), 2.56 (2 H, t, J = 6.0 Hz), 1.64–1.40 (1 H, m), 1.37 (3 H, d, J = 7.0 Hz), 1.33 (3 H, s), 0.83 (3 H, s)	

[a] Ar is syn or anti with respect to dimethyl groups.

Table XI. NMR and MS Data of 1,2-Diaryl-1-(methoxycarbonyl)cyclopropanes (**23**)

			NMR, δ			MS:
Y in **23**	(syn/ anti)[a]	mp	Ar	OMe	other	m/e (rel intensity)
4-Me	(syn)	*b*	7.94 (2 H, d, J = 8.0 Hz), 7.15 (2 H, d, J = 8.0 Hz), 6.87 (2 H, d, J = 8.0 Hz), 6.65 (2 H, d, J = 8.0 Hz)	3.67 (3 H, s)	3.17 (1 H, dd, J = 8.0, 9.0 Hz), 2.25–2.12 (1 H, m), 2.20 (3 H, s), 1.90 (1 H, dd, J = 6.0, 9.0 Hz)	311 (M^+, 95), 279 (100), 252 (80), 135 (92)
	(anti)	*b*	8.18 (2 H, d, J = 8.0 Hz), 7.63 (2 H, d, J = 8.0 Hz), 7.25–7.07 (4 H, m)	3.33 (3 H, s)	2.85 (1 H, dd, J = 8.0, 9.0 Hz), 2.47–2.30 (1 H, m), 2.33 (3 H, s), 1.65 (1 H, dd, J = 6.0, 9.0 Hz)	
H	(syn)	*b*	7.90 (2 H, d, J = 8.0 Hz), 7.21–6.96 (5 H, m), 6.75–6.63 (2 H, m)	3.61 (3 H, s)	3.10 (1 H, dd, J = 8.0, 8.0 Hz), 2.15 (1 H, dd, J = 6.0, 8.0 Hz), 1.96 (1 H, dd, J = 6.0, 8.0 Hz)	297 (M^+, 72), 265 (58), 237 (40)
	(anti)	*b*	8.10 (2 H, d, J = 8.0 Hz), 7.53 (2 H, d, J = 8.0 Hz), 7.17 (5 H, s)	3.20 (3 H, s)	2.74 (1 H, dd, J = 8.0, 8.0 Hz), 2.32 (1 H, dd, J = 6.0, 8.0 Hz), 1.53 (1 H, dd, J = 6.0, 8.0 Hz)	192 (60), 191 (58), 121 (100)
4-Cl	(syn)	180.5–184.0°	7.95 (2 H, d, J = 8.0 Hz), 7.13 (2 H, d, J = 8.0 Hz), 7.00 (2 H, d, J = 8.0 Hz), 6.65 (2 H, d, J = 8.0 Hz)	3.65 (3 H, s)	3.14 (1 H, dd, J = 7.0, 9.0 Hz), 2.20 (1 H, dd, J = 5.0, 7.0 Hz), 1.88 (1 H, dd, J = 5.0, 9.0 Hz)	333 (M + 2, 20), 331 (M^+, 65), 299 (46), 272 (42)
	(anti)	103.0–104.5°	8.14 (2 H, d, J = 8.0 Hz), 7.56 (2 H, d, J = 8.0 Hz), 7.20 (4 H, s)	3.32 (3 H, s)	2.82 (1 H, dd, J = 7.0, 9.0 Hz), 2.37 (1 H, dd, J = 5.0, 7.0 Hz), 1.68 (1 H, dd, J = 5.0, 9.0 Hz)	189 (54), 155 (100)
4-Br	(syn)	187.0–188.5°	7.96 (2 H, d, J = 8.0 Hz), 7.16 (2 H, d, J = 8.0 Hz), 7.14 (2 H, d, J = 8.0 Hz), 6.63 (2 H, d, J = 8.0 Hz)	3.65 (3 H, s)	3.13 (1 H, dd, J = 7.0, 9.0 Hz), 2.12 (1 H, dd, J = 6.0, 9.0 Hz), 1.89 (1 H, dd, J = 6.0, 7.0 Hz)	377 (M + 2, 73), 375 (M^+, 73), 237 (76), 218 (77), 201 (83), 199 (85), 89 (100)
	(anti)	102.0–106.0°	8.18 (2 H, d, J = 8.0 Hz), 7.60 (2 H, d, J = 8.0 Hz), 7.43 (2 H, d, J = 8.0 Hz), 7.18 (2 H, d, J = 8.0 Hz)	3.35 (3 H, s)	2.82 (1 H, dd, J = 7.0, 9.0 Hz), 2.39 (1 H, dd, J = 6.0, 7.0 Hz), 1.69 (1 H, dd, J = 6.0, 9.0 Hz)	
4-CN	(syn)	*b*	7.95 (2 H, d, J = 8.0 Hz), 7.33 (2 H, d, J = 8.0 Hz), 7.15 (2 H, d, J = 8.0 Hz), 6.84 (2 H, d, J = 8.0 Hz)	3.69 (3 H, s)	3.22 (1 H, dd, J = 4.0, 4.0 Hz), 2.33–2.19 (1 H, m), 2.10–1.95 (1 H, m)	322 (M^+, 100), 290 (45), 263 (20), 217 (44), 146 (62)
	(anti)	*b*	8.16 (2 H, d, J = 8.0 Hz), 7.62–7.45 (6 H, m)	3.33 (3 H, s)	2.84 (1 H, dd, J = 4.0, 4.0 Hz), 2.55–2.40 (1 H, m), 1.67 (1 H, dd, J = 3.0, 4.0 Hz)	
4-NO_2	(syn)	175.0–178.0°	7.95 (2 H, d, J = 8.0 Hz), 7.86 (2 H, d, J = 8.0 Hz), 7.15 (2 H, d, J = 8.0 Hz), 6.87 (2 H, d, J = 8.0 Hz)	3.66 (3 H, s)	3.28 (1 H, dd, J = 4.0, 4.0 Hz), 2.37–1.96 (2 H, m)	342 (M^+, 34), 325 (79), 237 (44), 189 (80), 166 (68), 150 (100)
	(anti)	*b*	8.15 (2 H, d, J = 8.0 Hz), 8.12 (2 H, d, J = 8.0 Hz), 7.58 (2 H, d, J = 8.0 Hz), 7.46 (2 H, d, J = 8.0 Hz)	3.34 (3 H, s)	2.92 (1 H, dd, J = 4.0, 4.0 Hz), 2.48 (1 H, dd, J = 4.0, 6.0 Hz), 1.80 (1 H, dd, J = 4.0, 6.0 Hz)	

[a] Ar is syn or anti with respect to Ar′. [b] Liquid.

(2 H, d, *J* = 8.5 Hz), 3.50 (1 H, s), 3.70 (3 H, s), 2.52 (1 H, q, *J* = 7.0 Hz), 2.48 (1 H, q, *J* = 7.0 Hz), 1.22 (3 H, t, *J* = 7.0 Hz); MS *m/e* (rel intensity) 255 (M^+, 3), 196 (100), 195 (71).

The Cyclopropane (20) from 2a and α-Chloroacrylonitrile. A solution of the diazo ester (**1a**, 50 mg) in the acrylonitrile (5 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC ($CHCl_3$–*n*-hexane = 1:1). Removal of the mobile phase under reduced pressure afforded 1-chloro-1-cyano-2-(methoxycarbonyl)-2-(4-nitrophenyl)cyclopropanes (**20**). The major isomer (43 mg, 67.0%) eluted first, followed by the minor isomer (16 mg, 25.0%). The major isomer: NMR (δ, $CDCl_3$) 8.25 (2 H, d, *J* = 8.0 Hz), 7.68 (2 H, d, *J* = 8.0 Hz), 3.79 (3 H, s), 2.68 (1 H, d, *J* = 7.5 Hz), 2.35 (1 H, d, *J* = 7.5 Hz); MS *m/e* (rel intensity) 280 (M^+, 34), 140 (64), 59 (100). The minor isomer: NMR (δ, $CDCl_3$) 8.25 (2 H, d, *J* = 8.0 Hz), 7.55 (2 H, d, *J* = 8.0 Hz), 3.80 (3 H, s), 2.92 (1 H, d, *J* = 7.5 Hz), 2.13 (1 H, d, *J* = 7.5 Hz); MS *m/e* (rel intensity) 280 (M^+, 34), 140 (64), 59 (100). Anal. Calcd for $C_{12}H_9N_2O_4Cl$: C, 51.35; H, 3.23; N, 9.98. Found: C, 51.72; H, 3.16; N, 9.90.

The Cyclopropanes (21) from 2a and 1-Hexene. A solution of the diazo ester (**1a**, 50 mg) in 1-hexene (3 mL) in a Pyrex tube was irradiated as described above and the reaction mixture was separated by preparative TLC ($CHCl_3$–*n*-hexane = 1:4) to give 1-(methoxycarbonyl)-1-(4-nitrophenyl)-2-butylcyclopropanes (**21**). (Syn-CO_2Me)-**21**: 20 mg (31.8%); NMR (δ, $CDCl_3$) 8.10 (2 H, d, *J* = 8.0 Hz), 7.45 (2 H, d, *J* = 8.0 Hz), 3.62 (3 H, s), 1.63–0.92 (12 H, m); MS *m/e* (rel intensity) 2.77 (M^+, 37), 208 (100), 176 (62), 148 (89). (Anti-CO_2Me)-**21**: 12 mg (18.8%); NMR (δ, $CDCl_3$) 8.15 (2 H, d, *J* = 8.0 Hz), 7.40 (2 H, d, *J* = 8.0 Hz), 3.60 (3 H, s), 1.82–0.80 (12 H, m); MS *m/e* (rel intensity) 277 (M^+, 37), 208 (100), 176 (62), 148 (89).

The Cyclopropanes (23) from 2 and Substituted Styrenes (22). A solution of **1a** and **1c** (50 mg) in substituted styrenes (**22**, 200 mg) and benzene (0.2 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC ($CHCl_3$–*n*-hexane = 2:3) to give isomeric pure 1,2-diaryl-1-(methoxycarbonyl)cyclopropanes (**23**). The isomer ratio was roughly 1:1 and overall yields were about 80–90% in each runs. The NMR and mass spectra of each isomer are given in Table XI together with the melting points.

Anal. **23** (Y = 4-Me) Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.67; H, 5.47; N, 4.41.

Anal. **23** (Y = H) Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.88; H, 5.06; N, 4.53.

Anal. **23** (Y = 4-Cl) Calcd for $C_{17}H_{14}NO_4Cl$: C, 61.55; H, 4.25; N, 4.22. Found: C, 61.04; H, 4.12; N, 4.04.

Anal. **23** (Y = 4-Br) Calcd for $C_{17}H_{14}NO_4Br$: C, 54.28; H, 3.75; N, 3.72. Found: C, 54.95; H, 3.53; N, 3.53.

Anal. **23** (Y = 4-CN) Calcd for $C_{18}H_{14}N_2O_4$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.05; H, 4.29; N, 8.65.

Anal. **23** (Y = 4-NO_2) Calcd for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.90; H, 4.10; N, 8.11.

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Triangulanes: Stereoisomerism and General Method of Synthesis

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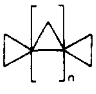
Abstract: The class of spirocondensed cyclopropanes, triangulanes, is defined and stereochemical problems of unbranched triangulanes (UTs) are considered from an algebraic-combinatorial point of view. The general method of triangulane synthesis that consists of the addition of chloromethylcarbene to methylenecyclopropanes with subsequent dehydrochlorination and final cyclopropanation of the resulting methylenetriangulanes is suggested and realized for [5]- and [6]-members of the family.

In the period of just over 90 years since spiropentane (**1**) was prepared[1] the spirocondensed three-membered ring systems, with their destabilization energy over of 65 kcal/mol,[2,3] have been the subject of numerous theoretical[2-5] investigations. We define "triangulanes" as the class of hydrocarbons whose skeleton is constructed exclusively from spiro-attached three-membered rings. The simplest subclass, that of *unbranched* triangulanes (UTs), may be represented with general formula **2**.[9] The parent hydrocarbon **1** (or [2]-triangulane),[1-3] as well as the [3]-[6,7d] and [4]-[6,7c] members of the family, have been synthesized up to date.

1



2

3

In this paper we shall deal exclusively with UTs and address ourselves to two specific topics: (i) enumeration problems and stereoisomerism of UTs and (ii) general synthetic method of UTs.

Stereochemical Problems of Unbranched Triangulanes. Three-membered rings of spiropentane (**1**) occupy two mutually

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