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Effect of Cations and Solvents on the S_N2 and S_N2' Product Distribution in the Reaction of 4-Bromo-3,5,5-trimethylcyclohex-2-enone with Pivalate Salts. 2. Evidence for a Concerted S_N2' Reaction on a Covalently Bonded Substrate

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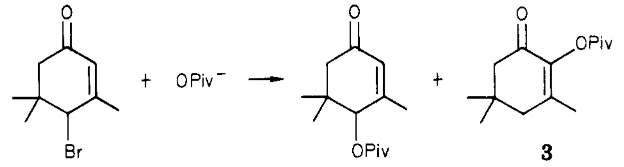
4-Bromoisophorone (1) undergoes nucleophilic displacement with pivalate salts at a faster rate in dipolar aprotic solvents than in protic solvents. In protic solvents only the S_N2' product is obtained, whereas in dipolar aprotic solvents, mixtures of S_N2' and S_N2 products are obtained with the ratio depending on the counterion and the solvent. In protic solvents the order of relative rates of MOPiv based on disappearance of 1 was in the order of increasing size of the counterion, $Et_4N^+ > K^+ \gtrsim Na^+ > Li^+$. In dipolar aprotic solvents the order of relative rates, $K^+ \gtrsim Li^+ > Na^+ > Et_4N^+$, did not show the expected dependence on the size of the counterion. The variation of the product ratio is rationalized in terms of the effect of solvation and ion pairing on the reactivity of $OPiv^-$, and it appears that an increase in reactivity of $OPiv^-$ favors displacement at C_4 (S_N2 pathway) more than displacement at C_2 (S_N2' pathway). The results suggest S_N2 and S_N2' attacks occur on a covalently bonded substrate rather than on a preformed tight ion pair.

We recently reported[2] that 4-bromoisophorone (1) reacts with pivalate ($OPiv^-$) salts in dipolar aprotic solvents to give a mixture of 4- and 2-pivaloxyisophorone (2 and 3, respectively, eq 1). This was the first report of an uncatalyzed direct S_N2 displacement at C_4 of 1. Heretofore, the only reported C_4 substitutions with 1 were catalyzed by silver salts such as silver acetate.[3] But these results have been disputed, the claim being that only C_2 attack occurred.[4] All previously studied nucleophiles such as HO^-[4], ArO^-[4], ArS^-[5] and $ArSO_2^-$[5], react only at C_2, giving an intermediate S_N2' product, 4, which is isomerized under the reaction conditions to the conjugated product 3, as shown for reaction with $OPiv^-$ (eq 2). We also demonstrated that the products 2 and 3 arise from direct S_N2 and S_N2' mechanisms, respectively, rather than through a carbanion intermediate. Privalate ion was chosen because, being a weak base, it is not likely to initiate reaction by formation of a carbanion at C_4, C_2, or the C_3 Me group. It is also a hard base and not likely to displace on the C_4 bromine atom to form a stabilized carbanion.



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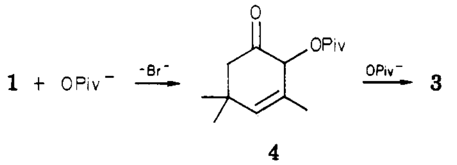

4 (2)

Table I. Reaction of 1 with KOPiv in Various Solvents for 40.5 h at 45 °C[a]

solvent	% yield recovd 1	 3 (S_N2')	 2 (S_N2)
HOPiv	75	25	
Me_2SO		34	66
DMF		29	71
$DMF-H_2O$ (9:1 v/v)	35	45	13
HMPA			90

[a] 5 mL of each solvent; 1.3 equiv of salt.

This paper is concerned with the variations in the rate of disappearance of 1 and in the ratio of S_N2'/S_N2 reactions as the counterion and solvent are altered. The solvents employed were pivalic acid (HOPiv), a protic solvent of low polarity, and the dipolar aprotic solvents dimethyl sulfoxide (Me_2SO), dimethyl formamide (DMF), and hexamethylphosphoramide (HMPA). A few experiments were also performed in DMF with added water (9:1 v/v). The counterions of $OPiv^-$ were Li^+, Na^+, K^+, $(C_2H_5)_4N^+$, and, in on instance, Ag^+.

Results and Discussion

Effect of Solvent. The effect of solvent was ascertained by comparing the reactions of KOPiv with 1 as summarized in Table I. The trend observed for potassium salts was much the same with the other counterions as seen from Table III. All experiments were performed at least in duplicate, and yields, based on NMR spectral analysis as described in our earlier paper[2], can be considered accurate to within ±3%.

From the percentage of recovered 1, 75% in HOPiv, 35% in $DMF-H_2O$ (9:18 v/v), and 0% in the aprotic solvents, it is apparent that protic solvents retard the rate of disappearance of 1. Rate retardation in protic solvents is to be expected because typically the anion, $OPiv^-$, suffers from reduced reactivity because of hydrogen bonding. This is especially true for the $DMF-H_2O$ (9:1, v/v) mixture. In HOPiv, a protic solvent with a fairly low dielectric constant (less than 10), the reactivity of $OPiv^-$ is reduced because some ions are ion paired with the counterion and the remainder hydrogen bond to HOPiv. In aprotic polar sol-

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[1] Taken in part from the Ph.D Thesis of S.J.J., City University of New York, 1973.

[2] H. Meislich and S. Jasne, *J. Org. Chem.*, 40, 2662 (1975).

[3] A. J. B. Edgar, S. H. Harper, and M. A. Kazi, *J. Chem. Soc.*, 1083 (1957).

[4] J. N. Marx, A. W. Carnrick, and J. H. Cox, *J. Org. Chem.* 37, 2308 (1972).

[5] L. D. Markley, *J. Org. Chem.*, 38, 3417 (1973).

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Table II. Yields of Products of Reaction of 1 with Pivalate Salts in HOPiv[a] for 40.5 h at 45 °C

	% yield[b]		
cation	recovd 1	3	4
Li^+	100		
Na^+	71	29	
K^+	75	25	
Et_4N^+	54	46	
Ag^+	65	10	25

[a] 5 mL of HOPiv, 1.3 equiv of each salt. [b] No **2** was obtained in any case.

Table III. Product Yields from the Reaction of 1 with MOPiv in Aprotic Solvents[a]

			% yield		
expt	cation, M^+	solvent	3 (S_N2')	2 (S_N2)	recovd 1
1	Li	Me_2SO	~100		trace
2	Na	Me_2SO	47	36	17
3	K	Me_2SO	34	66	
4	Et_4N	Me_2SO	17	58	25
5	Li	DMF	~100		trace
6	Na	DMF	46	18	36
7	K	DMF	29	71	
8	Et_4N	DMF	17	59	24
9	Li	HMPA	54	46	
10	K	HMPA		~100	
11	Et_4N	HMPA	26	16	23

[a] 5 mL of each solvent; 1.3 equiv of salt for 40.5 h at 45 °C.

vents, $OPiv^-$, typical of anions, is very poorly solvated, is weakly ion paired[6], and hence is freer and more reactive.

Another trend can be noticed from Table I; in the protic solvents (HOPiv and $DMF-H_2O$), **3**, the product from S_N2' attack, predominates over **2**, the product from S_N2 attack. As can be seen from Table II, regardless of the counterion used with $OPiv^-$ in HOPiv, no **2** was observed. The preference for reaction at C_2 (S_N2') rather than at C_4 (S_N2) in a protic solvent or one of low polarity can be rationalized on the basis of steric effects. The C_4 site is neopentyl-like and hindered whereas C_2 is more exposed to nucleophilic attack. Hence, reaction at C_4 should be more susceptible to the size of the nucleophile than should be reaction at C_2. Solvation by hydrogen bonding with protic solvents or intimate ion pairing in solvents of low polarity increases the effective sizes of anions. Therefore, it is not surprising that such solvents inhibit the S_N2 reaction at C_4 more than they inhibit the S_N2' reaction at C_2.

Significant differences in product distribution were observed with different counterions in the aprotic solvents as summarized in Table III. The novel observation was the direct substitution at C_4 to afford **2**. By proper selection of cation and solvent, the reaction can be directed to **2** almost exclusively (KOPiv in HMPA, expt 10) or exclusively to **3** (LiOPiv in Me_2SO or DMF, expts 1 and 5).

The appearance of **2** in dipolar aprotic solvents in even greater yield than **3** signals that the increased rate of disappearance of **1** was reflected mainly in an increase in the rate of the S_N2 reaction at C_4. This was especially true in HMPA where only **2** (S_N2) was isolated. Apparently, *the S_N2 pathway is favored more than the S_N2' pathway as $OPiv^-$ becomes more reactive.* The results obtained when water, a protic substance, was added to DMF (Table I) support this conclusion. The decrease in the rate of consumption of **1** was accompanied by a decrease in yield of **2** and a increase in the yield of **3**.

The data in Table III also show a significant difference in product distribution when **1** reacts with LiOPiv or with KOPiv in the three dipolar aprotic solvents. On changing from Me_2SO or DMF to HMPA for either salt, there is an increase in the yield of **2** to the expense of **3** (Table III, expts 1, 5, 9 and 3, 7, 10). These results substantiate our contention that as $OPiv^-$ becomes more reactive the ratio of S_N2 attack at C_4 to S_N2' attack at C_2 increases. It has been shown [7] that the rate of alkylation of a potassium carboxylate salt (3,3-dimethyl-2-ethyl butanoate) with an alkyl halide (1-chlorohexane) was faster in HMPA than in either Me_2SO or DMF. This result was used to suggest that of the three solvents, HMPA solvates K^+ most effectively, leaving the most reactive carboxylate anion. It is noteworthy that in the protic solvent, ethanol, no alkylation occurred. Owensby and Parker[8] observed that the order of increasing effectiveness of the solvent on carboxylate anion reactivity paralleled the order of their corresponding K^+ solvation potential. The greater cation separation, induced by more effective solvation of the counterion, generated a more reactive $RCOO^-$. HMPA had the highest K^+ solvation potential of the 15 common dipolar aprotic solvents used.

Szwarc[9] claims that the solvating power of aprotic solvents depends on "donicity", a measure of cation solvation, rather than on the dielectric constant. The donicities and dielectric constants (in parentheses) for these three solvents are as follows: Me_2SO, 29.8 (46.6); DMF, 30.9 (36.7); HMPA, 38.8 (30). Although HMPA has the lowest dielectric constant, it nevertheless has the largest donicity value and is the best cation solvator. In both Me_2SO and DMF, solvents with almost the same donicities, the product distribution was about the same. With KOPiv the slight difference in yield of **2** in DMF (71%) and Me_2SO (66%) is in accord with the donicity order of these solvents.

In contrast, Et_4NOPiv did not show this variance of product distribution with a change of solvent (Table III, expts 4, 8, and 11). Et_4N^+ differs from Li^+ and K^+ in being larger and in having its charge buried on the nitrogen atom and shielded by the four ethyl groups. Consequently, there could be a "leveling out" of the cation–solvation effectiveness of the solvent. The anion is in the same condition and has the same reactivity in each solvent so that the product distribution is invariant. This result also shows that the product distribution is little influenced by the difference in the dielectric constants of these solvents. A constancy of the rate of reaction with quaternary ammonium salts in different aprotic solvents was also observed during the alkylation of phenoxides. When K^+ was the counterion there were very significant changes in rate as donicities of the aprotic solvents changed.[10]

Effect of Cation. The main factor in determining the rate and product distribution is the reactivity of the anion, $OPiv^-$. Cations influence anion reactivity by ion pairing, and although the extent of ion pairing is affected by the solvent, certain trends are discernible when the cations are changed in a fixed solvent.

An ion-paired cation can also exert a unique catalytic role in our system. The ion-paired salt which is in equilibrium with dissociated ions may coordinate through M^+ with the carbonyl oxygen atom of **1** to give intermediate

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(6) A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962).

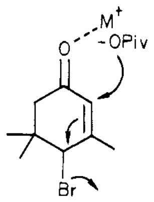
(7) P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, **41**, 1373 (1976).

(8) D. A. Owensby, A. J. Parker, and J. W. Diggle, *J. Am. Chem. Soc.*, **96**, 2612 (1974).

(9) M. Szwarc, "Ions and Ion Pairs in Organic Reactions"; Wiley-Interscience: New York, 1972; Vol. 1 pp 5–6.

(10) J. Ugelstad, T. Ellingsen, and A. Berge, *Acta Chem. Scand.*, **20**, 1593 (1960).

5. Now reaction of $OPiv^-$ at C_2 is intramolecular as shown,



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and faster than an intermolecular reaction at C_4. Intermediate 5 should be of little importance in protic solvents where hydrogen bonding between the oxygen atom and solvent would prevail. Hydrogen bonding of 1 with a particular protic solvent would be a constant effect independent of the cation. Water could be a unique protic solvent in that a single molecule could form a hydrogen bond with the anion and with the carbonyl oxygen atom and in this way assume the role of M^+ in 5. This effect of water might account in part for the increase in yield in 3 at the expense of 2 when water was added to DMF (Table I).

We first consider effects on the relative rate of consumption of 1. In the low-polarity, protic solvent (HOPiv), in which ion pairing may also occur, the order of relative rates for different cations based on recovered unreacted 1 is $Li^+ \ll Na^+, K^+ < Et_4N^+$ (Table II). This order is directly related to the size of the cation: *as the size of the cation increases, the rate of reaction increases.* These results, in turn, are interpretable in terms of the reactivity of the anion because as the size of its counterion increases, $OPiv^-$ becomes less associated and more reactive. $OPiv^-$ is tightly bound by Li^+, and no reaction is observed with LiOPiv. On the other hand, $OPiv^-$ is least tightly bound by Et_4N^+, and maximum reaction of 1 is observed with Et_4NOPiv.

Studies of C vs. O alkylations with acetoacetic ester[11] and naphthoxide[12] also showed that Li^+ coordinates better with the oxygen atom of anions than do the other alkali metal or quaternary ammonium cations. The reaction with AgOPiv is not comparable with those with the other salts in Table II because AgOPiv is not completely soluble in HOPiv. A heterogeneous reaction could have occurred on the surface of the salt to account for the isolation of 4. Since much of the $OPiv^-$ is immobilized on the solid surface, it cannot easily initiate reconjugation of 4 to 2.

The orderly relationship of the rate of reaction of 1 and the size of the cation is absent in the dipolar aprotic solvents. The observed average order was $K^+ \gtrsim Li^+ > Na^+$, Et_4N^+. An earlier report on the alkylation of alkali metal salts of 2-methyl-2-propylpentanoate with 1-iodopentane in dipolar aprotic solvents gave a regular order of reactivity based on the size of the cation $Cs^+ > K^+ > Na^+ > Li^+$. This order was attributed to an increase in ion pairing of the carboxylate anion and cation as the size of the cation decreases[7]. One irregularity in our order of reactivity that requires explanation is the enhanced reactivity of the Li^+ salt. We speculate that when $M^+ = Li^+$, 5 is a significant intermediate so that Li^+ behaves as a catalyst. Such a catalytic role is not possible when carboxylate salts are alkylated with simple alkyl halides.

The other apparent irregularity in our order is the diminished reactivity of the Et_4N^+ salt. Apparently, Et_4NOPiv is *not* the least ion paired of the salts in all solvents. Our result is understandable when the following equilibrium in polar aprotic solvents (eq 3) is considered.

$$\underset{\substack{\text{ion pair with}\\ \text{variable}\\ \text{coulombic}\\ \text{attraction}}}{(\mathrm{M^+OPiv^-})} \rightleftharpoons \underset{\substack{\text{of varying}\\ \text{strength}\\ \text{of solvation}}}{\mathrm{M^+}\ (\text{solvated})} + \underset{\substack{\text{free ion}\\ \text{(insignificant}\\ \text{solvation)}}}{\mathrm{OPiv^-}} \qquad (3)$$

On increasing the size of the counterion, the coulombic attraction of the ion pair is weakened but concomitantly so is the solvation of M^+. In going from Li^+ to Na^+ to K^+ the weakening of the coulombic attraction of the ion-pair dominates over the weakening of the solvation of M^+. Hence, the equilbrium shifts more to the right, giving a freer, more reactive $OPiv^-$. With Et_4N^+ the weakening of the solvation becomes more significant, and the equilbrium shifts to the left. With Et_4N^+ more $OPiv^-$ is tied up as an ion pair, albeit one with a weak electrostatic attraction, and consequently $OPiv^-$ suffers a loss of reactivity. We emphasize that this phenomenon occurs only in polar, aprotic solvents. With solvents in which solvation of the cation is minimal, R_4N^+ salts would be the least ion paired.

There is a considerable amount of evidence in the literature to substantiate our contention about the ion pairing of quaternary ammonium salts in polar aprotic solvents. Much of this evidence comes from conductivity measurements which indicate that R_4N^+ salts of $B(C_6H_5)_4^-$ [13] and I^- [14,15] were poorer conductors than Na^+ [13,14] salts or Li^+ salts.[15] Heathcock and his co-workers[16] in their studies on stereoselective aldol condensations showed that R_4N^+ enolates in THF give the same kinetic stereoselectivity as the Li^+ enolates and that both ions were more effective in maintaining the stereoselectivity than was K^+. They suggest that although the R_4N^+ cannot participate in a ligand association with the two oxygen atoms, the coulombic attraction could be sufficient to organize the transition state permitting the high selectivity.

We now turn our attention to the effect the cation has on the product distribution. The experiment sets 1–3 and 5–7 in Table III indicate that in aprotic solvents the yield of 3 declines with a concurrent increase in the yield of 2 as the size of the cation increases (Li^+ to Na^+ to K^+). These results are consistent with our generalization that an increase in reactivity of $OPiv^-$ enhances the S_N2 rate more than the S_N2' rate. As the alkali metal counterion gets smaller, there is more intimate or solvent-separated ion pairing[17] and therefore more diminution in the reactivity of the anion. The exclusive formation of 3 in Me_2SO and DMF when Li^+ is the counterion can also be rationalized in part by the intermediacy of 5 when $M^+ = Li^+$. It is noteworthy that when LiOPiv is reacted with 1 in HMPA, the yield of 3 declines and the yield of 2 rises (expt 9, Table III). The association of Li^+ is more effective with HMPA than with Me_2SO of DMF. This affords a more reactive $OPiv^-$ and also inhibits formation of 5 which results in an increase of the ratio of S_N2/S_N2' pathways.

Conclusion

The consistent, novel observation that emerges from this study is the augmentation of the S_N2 product/S_N2' product

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[11] W. J. Noble and C. H. F. Morris, *J. Org. Chem.*, 34, 1969 (1969).

[12] N. Kornblum, R. Seltzer, and S. Haberfield, *J. Am. Chem. Soc.*, 85, 1148 (1963).

[13] C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 87, 5548 (1965).

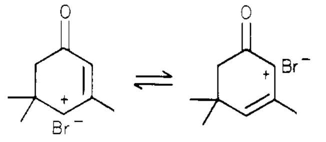
[14] N. K. Levitskaya, L. I. Tkachenko, and A. M. Shkodin, *Electrokhimija*, 10, 580 (1974); *Chem. Abstr.*, 81, 30442 (1974).

[15] U. Mayer, V. Gutmann, and A. Lodzinska, *Monatsch. Chem.*, 104, 1045 (1973).

[16] C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, and J. Lampe, *J. Org. Chem.*, 45, 1066 (1980).

[17] J. F. Coetzee and C. D. Ritchie, "Solute-Solvent Interaction", Marcel Dekker, New York, 1969, p 275.

ratio as the reactivity ("freeness") of OPiv$^-$ increases. This finding bears on the question of whether **1** first forms a tight ion pair. Bordwell[18] has suggested that S_N2' and many S_N2 reactions proceed through intermediate tight ion pairs. Sneen[19] showed that competitive S_N2 and S_N2' reactions follow from intermediate, equilibrating, tight ion pairs. Bordwell and Pagani[20] suggest an intermediate ion pair with a delocalized carbocation and a centered, leaving group ion. For **1** the equilibrating tight ion pairs would be **6** and **7**, and the delocalized carbocation pair would be **8**. In our earlier paper[2], the observance of a negative salt effect raised doubt of the intermediacy of a tight ion pair in these reported reactions of **1**. This doubt is now reinforced by the fact that the S_N2 rate increased more than did the S_N2' rate as OPiv$^-$ became more reactive. Bordwell and Pagani[20] reported that allylic bromides such as $ArSO_2CH{=}CHC(CH_3)_2Br$, which react through a tight ion pair, gave the *same* amount of S_N2 and S_N2' product regardless of the nucleophile, the counterion, or the solvent used. The product ratio from ion-pair intermediates seems to depend on the relative stabilities of the products and not on the reactivity of the nucleophile.



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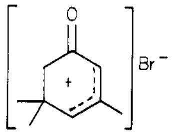

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Our results, however, are compatible with reaction of a covalently bonded substrate. In such a substrate the electron densities on C_2 and C_4 are very different, and the extent of reaction at each site should change differently as the reactivity of the nucleophilic anion changed. The π-bonded C_2 atom is electron rich, and as OPiv$^-$ becomes more reactive the expected rate enhancement for attack at C_2 is attenuated by the increased repulsive force between the anion and the carbon site. Unlike C_2, C_4 is not electron rich but may actually be somewhat electron poor because of the presence of the electron-withdrawing bromine atom. Therefore, the heightened reactivity of OPiv$^-$ should result in an enhanced rate at C_4, notwithstanding the steric hindrance. In accord with Sneen's[19] observations, we discount the possibility that the S_N2' reaction proceeds through an ion pair while the S_N2 reaction does not.

The uniqueness of **1** in undergoing an S_N2' reaction without first forming an ion pair may be because of the high energy of **6**, **7**, or **8** resulting from adjacent positive charges on C_2 and on the carbonyl carbon.

Experimental Section

The syntheses of **1–3**, KOPiv, and AgOPiv are described in our earlier paper. NaOPiv, LiOPiv and Et_4NOPiv were prepared in the same way as was KOPiv. In the same paper are described the reactions of **1** with the pivalate salts and the NMR analysis of the products.

Registry No. 1, 16004-91-4; LiOPiv, 14271-99-9; NaOPiv, 1184-88-9; KOPiv, 19455-23-3; Et_4NOPiv, 16432-64-7; AgOPiv, 7324-58-5.

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[18] G. Bordwell, *Acc. Chem. Res.*, **8**, 281 (1970).

[19] (a) R. A. Sneen and W. A. Bradley, *J. Am. Chem. Soc.*, **94**, 6985 (1972); (b) R. A. Sneen and P. S. Kay, *ibid.*, **94**, 6983 (1972); (c) R. A. Sneen and J. V. Carter, *ibid.*, **94**, 6990 (1972).

[20] F. G. Bordwell and G. A. Pagani, *J. Am. Chem. Soc.*, **97**, 118 (1975).

Substituent Effects on the Regioselectivity of Intramolecular Carbene C–H Insertion. Cyclizations of 1- and 5-Substituted 2-Adamantylidenes[1]

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Carbenes, 1-methyl-, 1-chloro-, 5-methyl-, and 5-chloro-2-adamantylidene, were generated by pyrolysis of dry tosylhydrazone alkali salts. Each of these carbenes yielded both possible products of the intramolecular C–H insertion, the corresponding 1- and 3-substituted 2,4-didehydroadamantanes or 1- and 7-substituted 2,4-didehydroadamantanes. The product distribution varies considerably depending on the substituent and its position relative to the carbenic center. The results indicate that the regioselectivity of the intramolecular carbene C–H insertion is sensitive to *very small* changes in geometry and electron distribution in the system.

Intramolecular carbene reactions provide facile and frequently the only route to a number of interesting molecules.[2,3] Intramolecular cycloadditions to olefinic bonds have been used in preparations of various strained alicyclic systems[4] and, recently, small-ring propellanes.[5] Since only one olefinic bond is usually present in the molecule, the cycloaddition product, if stable, can easily be foreseen. However, the course of intramolecular carbene

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[1] Presented in part at the 6th and 7th Meetings of Chemists of Croatia, Feb 1979 and Feb 1981, Zagreb, Yugoslavia.

[2] (a) Jones, M., Jr.; Moss, R. A., Eds. "Carbenes"; Wiley-Interscience: New York, 1973; Vol. I. (b) Kirmse, W. "Carbene, Carbenoide und Carbenanaloge"; Verlag Chemie: Weinheim/Bergstr., Germany, 1969. (c) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1964. (d) Shapiro, R. H. *Org. React.* 1976, *23*, 405–508. (e) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

[3] Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

[4] Hamon, D. P. G.; Hopton, H. P. *Tetrahedron Lett.* **1973**, 1675. Tsuruta, H.; Kurabayashi, K.; Mukai, T. *Ibid.* **1967**, 3775. Closs, G. L.; Larrabee, R. B. *Ibid.* **1965**, 287. Lemal, D. M.; Shim, K. S. *Ibid.* **1964**, 3231. Doering, W. v. E.; Pomerantz, M. *Ibid.* **1964**, 961. Schwarz, M.; Besold, A.; Nelson, E. R. *J. Org. Chem.* **1965**, *30*, 2425. Masamune, S. *J. Am. Chem. Soc.* **1964**, *86*, 735. Closs, G. L.; Closs, L. E.; Böll, W. A. *Ibid.* **1963**, *85*, 3796. Lemal, D. M.; Menger, F.; Clark, G. W. *Ibid.* **1963**, *85*, 2529. Brinker, U. H.; Streu, J. *Angew. Chem.* **1980**, *92*, 641.

[5] Majerski-Mlinarič, K.; Majerski, Z. *J. Am. Chem. Soc.* **1980**, *102*, 1418; Hamon, D. P. G.; Trenerry, V. C. *Ibid.* **1981**, *103*, 4962.

0022-3263/82/1947-2520$01.25/0