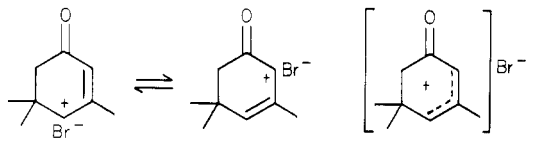
ratio as the reactivity ("freeness") of $OPiv^-$ increases. This finding bears on the question of whether **1** first forms a tight ion pair. Bordwell[18] has suggested that S_N2' and many S_N2 reactions proceed through intermediate tight ion pairs. Sneen[19] showed that competitive S_N2 and S_N2' reactions 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



6 **7** **8**

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.

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.

(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).

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.

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

Sanja Hiršl-Starčevič and Zdenko Majerski*

Rudjer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

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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

(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.

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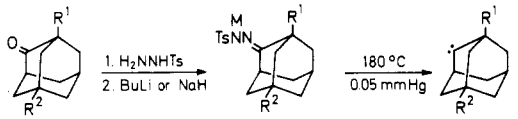
Table I. Observed and Calculated (in Parentheses) ^{13}C NMR Chemical Shifts in the Intramolecular C–H Insertion Products of Carbenes 4a-d

carbon[b]	^{13}C NMR chemical shifts[a]					
	8a	9a	10a	8b	9b	10b
C_1	33.3,*[c] d (33.2)	37.3, s (33.8)	33.4,* d (33.2)	34.9,*[c] d (35.5)	67.7, s (72.2)	36.0,* d (35.5)
C_2	33.1,*[c] d (31.4)	29.4,[c] d (31.4)	23.4,* d (23.7)	34.6,*[c] d (34.0)	28.9,[c] d (34.0)	22.5,* d (21.9)
C_3	25.0, s (22.2)	20.9, d (21.6)	23.7, d (21.6)	47.8, s (60.7)	24.3, d (24.0)	26.7, d (24.0)
C_4	33.1,*[c] d (31.4)	25.3, d (25.0)	23.4,* d (23.7)	34.6,*[c] d (34.0)	21.2, d (21.9)	22.5,* d (21.9)
C_5	33.3,*[c] d (33.2)	33.0[c] (33.2)	33.4,* d (33.2)	34.9,*[c] d (35.5)	32.2,[c] d (35.5)	36.0*, d (35.5)
C_6	33.7,* t (32.9)	32.8[c] (32.9)	40.7,* t (40.5)	32.3,* t (31.2)	31.2, t (31.2)	43.6,* t (43.3)
C_7	27.9, d (27.8)	27.6,[c] d (27.8)	29.6, s (28.4)	28.9, d (30.2)	31.3, d (30.2)	68.9, s (67.0)
C_8	33.7,* t (32.9)	41.2, t (40.5)	40.7,* t (40.5)	32.3,* t (31.2)	43.7, t (43.3)	43.6,* t (43.3)
C_9	52.3, t (52.0)	59.2, t (59.7)	52.2, t (51.9)	50.3, t (50.3)	61.6, t (62.4)	51.2, t (50.3)
C_{10}	35.7, t (36.0)	29.1, t (28.3)	36.2, t (36.0)	37.5, t (38.8)	27.7, t (26.7)	38.9, t (38.8)
CH_3	26.4, q	27.5,[c] q	31.4, q			

[a] Observed chemical shifts in parts per million (in C_6D_6 for **8a–10a** and in $CDCl_3$ for **8b–10b**) and splitting patterns in the proton off-resonance spectra. Double-intensity signals in the quantitative spectra are denoted with an asterisk. The corresponding calculated chemical shifts[21] are given in parentheses. [b] The numbering of carbons refers to structures **8–10** (Scheme III). [c] Tentatively assigned chemical shifts.

Scheme I[a]

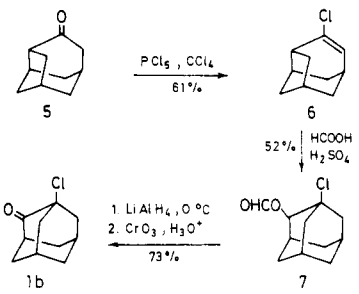


1a, $R^1=CH_3$; $R^2=H$ 2a,3a, $R^1=CH_3$; $R^2=H$ 4a, $R^1=CH_3$; $R^2=H$
b, $R^1=Cl$; $R^2=H$ b, $R^1=Cl$; $R^2=H$ b, $R^1=Cl$; $R^2=H$
c, $R^1=H$; $R^2=CH_3$ c, $R^1=H$; $R^2=CH_3$ c, $R^1=H$; $R^2=CH_3$
d, $R^1=H$; $R^2=Cl$ d, $R^1=H$; $R^2=Cl$ d, $R^1=H$; $R^2=Cl$

insertions into the C–H bond is frequently questionable. It appears to depend on a number of factors such as proximity[2] and orientation[6] of the C–H bonds relative to the carbenic center, as well as nucleophilicity and the type (tertiary, secondary, or primary) of C–H bonds in question.[7f-h] Most of these factors have been revealed by using carbenoids,[8] rather than free carbenes, and more or less conformationally flexible systems as models.[6,7] This has largely complicated the interpretations.

In this work we have studied substituent effects in the competitive intramolecular insertions of 1- and 5-substituted 2-adamantylidenes[9] (**4a,b** and **4c,d**). The carbenes were generated by thermal decomposition of dry tosylhydrazone alkali salts, the process known to produce free carbenes.[2] Owing to its rigidity and high symmetry, the adamantane system appears to be an ideal model for such studies. It is free from both the conformational complications and elimination reactions. The latter would lead to the highly strained and unstable anti-Bredt olefin, adamantene. Consequently, differences in reactivities of the various C–H bonds should result exclusively from substituent effects.

Scheme II



5 6 1b 7

Results and Discussion

We have studied here the regioselectivity in intramolecular C–H insertions of 1-methyl-2-adamantylidene (**4a**, Scheme I), 1-chloro-2-adamantylidene (**4b**), 5-methyl-2-adamantylidene (**4c**), and 5-chloro-2-adamantylidene (**4d**). Carbenes **4a–d** were generated by pyrolysis of tosylhydrazone alkali salts **3a–d** (Scheme I) in vacuo, and the products were collected in a trap cooled with liquid nitrogen. The salts were prepared (via tosylhydrazones **2a–d**) from the corresponding ketones, 1-methyl- (**1a**), 1-chloro- (**1b**), 5-methyl- (**1c**), and 5-chloro-2-adamantanone (**1d**), by standard procedures.[10]

Ketones **1a** and **1c** were obtained by starting from 4-protoadamantanone[11] and 1-methyladamantane,[12] respectively, and following the reported procedures.[13,14] 5-Chloro-2-adamantanone (**1d**) was readily derived from 5-hydroxy-2-adamantanone[15] by the reaction with thionyl chloride, but various attempts[16] to convert 1-hydroxy-2-

(6) (a) Hill, E. A. *J. Org. Chem.* **1972**, *37*, 4008. (b) Gutsche, C. D.; Bachman, G. L.; Udell, W.; Bäuerlein, S. *J. Am. Chem. Soc.* **1971**, *93*, 5172. (c) Kirmse, W.; Wächtershäuser, G. *Tetrahedron* **1966**, *22*, 63.

(7) (a) Kirmse, W.; Schladetsch, H. J.; Bücking, H.-W. *Chem. Ber.* **1966**, *99*, 2579. (b) Paquette, L. A.; Chamot, E.; Browne, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 637. (c) Paquette, L. A.; Taylor, R. T. *Ibid.* **1977**, *99*, 5708. (d) Baird, M. S. *J. Chem. Soc., Chem. Commun.* **1979**, 776. (e) Paquette, L. A.; Zon, G.; Taylor, R. T. *J. Org. Chem.* **1974**, *39*, 2677. (f) Moore, W. R.; King, B. J. *Ibid.* **1971**, *36*, 1877. (g) Reinarz, R. B.; Fonken, G. J. *Tetrahedron Lett.* **1973**, 4013. (h) Moore, W. R.; Hill, J. B. *Ibid.* **1970**, 4343.

(8) Goldstein, M. J.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 2293. Closs, G. L.; Moss, R. A. *Ibid.* **1964**, *86*, 4042.

(9) Very recently a work on intermolecular reactions of 2-adamantylidene has been reported (Moss, R. A.; Chang, Ming Jing *Tetrahedron Lett.* **1981**, 3749).

(10) Kaufman, G. M.; Smith, J. A.; Vander Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935.

(11) Majerski, Z.; Hameršak, Z. *Org. Synth.* **1979**, *59*, 147.

(12) Ōsawa, E.; Majerski, Z.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 205.

(13) (a) Cuddy, B. D.; Grant, D.; McKervey, M. A. *J. Chem. Soc. C*, **1971**, 3173. (b) Lenoir, D.; Glaser, R.; Mison, P.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1821.

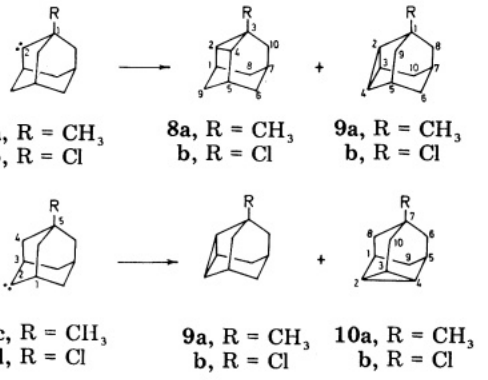
(14) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2644.

(15) Lavrova, L. N.; Klimova, N. V.; Smarjan, M. I.; Skoldinov, A. P. *Zh. Org. Khim.* **1976**, *12*, 2369. Geluk, H. W. *Synthesis* **1972**, 374.

(16) Treatment of 1-hydroxy-2-adamantanone with thionyl chloride alone, a mixture of thionyl chloride and polyphosphoric acid,[17] phosphorus pentachloride,[18] or dichlorocarbene generated from chloroform with aqueous NaOH in the presence of TEBA[19] produced various mixtures of unreacted starting hydroxy ketone and tarry materials.

(17) Kopecký, J.; Smejkal, J. *Tetrahedron Lett.* **1967**, 1931.

Scheme III



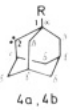
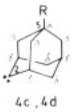
4a, R = CH_3 b, R = Cl; 8a, R = CH_3 b, R = Cl; 9a, R = CH_3 b, R = Cl

4c, R = CH_3 d, R = Cl; 9a, R = CH_3 b, R = Cl; 10a, R = CH_3 b, R = Cl

adamantanone[13a] to 1-chloro-2-adamantanone (**1b**) were unsuccessful in our hands. Ketone **1b** was finally prepared in 23% overall yield by starting from 4-protoadamantanone (**5**)[11] via 4-chloro-4-protoadamantene (**6**)[13b] and 1-chloro-2-(formyloxy)adamantane (**7**) as outlined in Scheme II. Starting ketones **1a–d** and tosylhydrazones **2a–d** were at least 96% pure (by GC and ^{13}C NMR).

Each of the carbenes **4a–d** yielded both possible products of the intramolecular insertion into the methylene C–H bonds[20] (Scheme III). 1-Methyl- (**4a**) and 1-chloro-2-adamantylidene (**4b**) produced mixtures of the corresponding 1- and 3-substituted 2,4-didehydroadamantanes (**8a + 9a**, **8b + 9b**), while 5-methyl- (**4c**) and 5-chloro-2-adamantylidene (**4d**) gave mixtures of the respective 1- and 7-substituted 2,4-didehydroadamantanes (**9a + 10a**, **9b + 10b**). The products derived from the chloro carbenes **4b** and **4d** were separated by column chromatography, while the product mixtures obtained from the methyl carbenes **4a** and **4c** could not be separated. These products were identified in the mixtures. The proofs for the structures of products are based on the mass spectra [m/e 148 (M^+), 133 ($M^+ - CH_3$) for **8a**, **9a**, and **10a**; m/e 168 (M^+), 133 ($M^+ - Cl$) for **8b**, **9b**, and **10b**], as well as the IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectra of all products showed the characteristic cyclopropane C–H streching absorption at 3040 or 3030 cm^{-1}, while the ^1H NMR spectra demonstrated the absence of olefinic protons. The ^1H NMR spectra of the product mixtures **8a + 9a** and **9a + 10a** showed two methyl singlets at δ 0.95 and 1.11 and at δ 1.11 and 0.79, respectively, the relative intensities of which indicated the product ratios. The most important information was obtained by ^{13}C NMR spectroscopy. In Table I are presented ^{13}C chemical shifts of all products (**8a–10a** and **8b–10b**), splitting patterns of the signals in the proton off-resonance spectra, and the relative signal intensities in the quantitative spectra, as well as the corresponding calculated chemical shifts (in parentheses). The latter are obtained by adding, to the ^{13}C chemical shifts of 2,4-didehydroadamantane, the differences between the corresponding chemical shifts of 1-methyl- and 1-chloroadamantane, respectively, and those of adamantane itself.[21] The calculated chemical shifts for all six products are in good agreement with the corresponding observed shifts, except for the carbon atoms bearing the substituent and the most proximate cyclopropane carbon(s), as well as carbon 5 in **9b**. These discrepancies arise probably from the nonadditivity of the substituent effects due to interactions of the substituent and the cyclopropane ring electrons. Similar interactions of the carbonyl π electrons and the substituent have been observed in a series of 4-substituted 2-adamantanones.[22]

Table II. Product Distributions in the Intramolecular C–H Insertions of Carbenes 4a–d

carbene	R	product distribution,[a] % 8	9	10
 4a, 4b	H[b]	50	50	
	CH_3[c]	78	22	
	Cl[d]	67	33	
 4c, 4d	H[b]		50	50
	CH_3[c]		26	74
	Cl[d]		8	92

[a] Average values of three to five independent pyrolyses with two to five GC and/or ^{13}C NMR analyses of each product mixture. The uncertainties (standard deviations) are ±1% for the products of the carbenes **4a,b,d** and ±2% for the products of **4c**. [b] For R = H, compounds **8** ≡ **9** ≡ **10**, and, therefore, by definition, the product distributions are written as 50:50. [c] A small amount of 1-methyladamantane (4–5%) was also detected. [d] 1-Chloroadamantane was detected in an amount of 1–2%.

The product distributions were determined by gas chromatography and quantitative ^{13}C NMR spectroscopy. The results are given in Table II. Each of the carbenes **4a–d** produces both possible products of the intramolecular insertion into the methylene C–H bonds, the corresponding 1- and 3-substituted 2,4-didehydroadamantanes or 1- and 7-substituted 2,4-didehydroadamantanes. However, the product ratio varies considerably depending on the substituent and its position relative to the carbenic center. The predominant products of the two 1-substituted 2-adamantylidenes (**4a,b**) are 3-substituted 2,4-didehydroadamantanes (**8a,b**), while those of the 5-substituted 2-adamantylidenes (**4c,d**) are 7-substituted 2,4-didehydroadamantanes (**10a,b**). The minor products of all four carbenes, **4a–d**, are the corresponding 1-substituted 2,4-didehydroadamantanes (**9a,b**). Since carbenes are, generally, highly reactive, unstable species, the transition state for the carbene C–H insertion should be relatively insensitive to the structure and stability of the products.[23] The product distributions could be explained, in part, by nonbonded repulsions present in the carbenes **4a–d** between the substituent and the proximate methylene hydrogen atoms (β, Table II), as well as between these methylene hydrogens and the more remote ones (δ). Such repulsions should change slightly the distances and steric arrangements of all hydrogen atoms relative to the carbenic center and lead to minor skeletal deformations.[24]

Investigation of a 2-adamantylidene model indicated that the introduction of a substituent at position 1 would increase the distance between the carbenic center and both the *syn*-δ-hydrogen and δ-carbon atoms (for the notation of atoms see Table II). The β-carbon atoms would move

(18) Bagal, M. L.; Klinduhova, T. K.; Lantvoev, V. I. *Zh. Org. Khim.* **1975**, *11*, 1645.
(19) Tabushi, I.; Yoshida, Z.; Takahashi, N. *J. Am. Chem. Soc.* **1971**, *93*, 1820.
(20) No product of the insertion into the methyl group was detected.
(21) For example, the α increment is added to the chemical shift of that carbon of 2,4-didehydroadamantane which will bear the substituent, β increments are added to the shifts of the adjacent carbons, and so forth.
(22) Duddeck, H. *Tetrahedron* **1978**, *34*, 247. Duddeck, H.; Wolff, P. *Org. Magn. Reson.* **1977**, *9*, 528.
(23) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
(24) Introduction of a bridgehead substituent in an adamantane molecule has been shown to change both the bond angles and bond lengths in the adamantane skeleton due to nonbonded interactions.[25]
(25) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. Alden, R. A.; Kraut, J.; Traylor, T. G. *Ibid.* **1968**, *90*, 74.

closer to the carbenic center, while the *syn*-β-hydrogen atoms would tilt toward the favorable[6a] coplanar arrangement of the C–H and the carbene p and hybrid orbitals. Introduction of a substituent at position 5 would decrease the distances between the carbenic center and both the *syn*-β- and *syn*-δ-hydrogen atoms. At the same time, the former ones would shift farther from the plane of the carbene p and hybrid orbitals, while the latter would move closer to this favorable[6a] arrangement. The skeletal deformations would decrease the distances between the carbenic center and the δ-carbon atoms and increase those between the carbenic center and the β-carbons. All these changes are very small but appear to be consistent with the preferred cyclization of the carbenes **4a** and **4b** to didehydroadamantanes **8** and cyclization of **4c** and **4d** to didehydroadamantanes **10**. The model investigation also revealed that the carbene p orbital was neither approximately collinear with the C–H bond being attacked[26] nor perpendicular to this bond at its midpoint,[6b] these two arrangements being claimed to be favorable for carbene C–H insertions. Owing to the geometry of the adamantane skeleton, the transition state is necessarily triangular.

The data presented in Table II indicate that both 1-methyl- *and* 1-chloro-2-adamantylidene (**4a,b**) attack preferably the hydrogen atoms closer to the substituent, while 1-methyl- *and* 1-chloro-5-adamantylidene (**4c,d**) prefer to attack the hydrogen atoms furthest from the substituent. This was explained by the steric effect, i.e., by nonbonded repulsions between the substituent and the hydrogen atoms, which change the distances and steric arrangements of all hydrogen atoms relative to the carbenic center (see above). However, both chloroadamantylidenes (**4b,d**) exhibit a somewhat greater tendency to attack the remote hydrogen atoms than the methyladamantylidenes **4a** and **4c**. Since the methyl group is larger than chlorine (the van der Waals radius of the former is 2.0 Å[27] and that of the latter 1.80 Å[28]), the source of this selectivity cannot be a steric effect. The results are, however, in accord with the inductive and field effects of the methyl group and chlorine. The electron-donating methyl group increases the nucleophilicity of the proximate C–H bonds,[7] while the electron-withdrawing chlorine has the opposite effect. The carbene, being an electrophile, will attack preferably the more nucleophilic C–H bonds. Since the C–H bonds under siege are situated rather far (at β- and δ-positions) from the substituent, these effects must be quite weak.

Carbenes **4a** and, particularly, **4d** are more selective than **4b** and **4c**. This can be explained by a combined operation of the steric and electronic effects. These effects operate in the same direction for the former two carbenes but in opposite directions for the latter two. The greater selectivity of **4d** compared with that of **4a** is in accord with the relative strengths of the electronic effect of chlorine and of the methyl group.[29]

In conclusion, the regioselectivity of the intramolecular carbene C–H insertion appears to be sensitive to *very small* changes in geometry[30] and electron distribution in the system. Such small changes necessarily lead to only minor changes in the free energy of activation. Yet the product distribution of the carbenes **4a–d** varies considerably with the substituent and its position relative to the carbenic center. This indicates that the free energy of activation for the carbene C–H insertion is very small.

Experimental Section

Purity of all compounds was controlled by GC or TLC. ^{13}C NMR spectra were taken on a JEOL FX-100 spectrometer, ^{1}H NMR spectra were obtained on a JEOL FX-90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were taken on a Varian CH-7 or a KRATOS MS25 mass spectrometer. GC analyses were carried out on a Varian Aerograph 940 or a Varian Aerograph M-1800 gas chromatograph by using stainless-steel analytical or capillary columns.

1-Methyl-2-adamantanone (1a) was prepared [≥98% pure by GC; diethylene glycol succinate (DEGS), 135 °C] in 81% overall yield from 4-protoadamantanone[11] by following the procedure described previously:[13] ^{13}C NMR ($CDCl_3$) δ 218.2 (s, 1 C), 46.7 (d, 1 C), 46.5 (t + s, 3 C), 39.3 (t, 2 C), 35.6 (t, 1 C), 28.2 (d, 2 C), 22.8 (q, 1 C). The ^{1}H NMR, IR, and mass spectra are in complete agreement with the reported data.[13]

1-Methyl-2-adamantanone Tosylhydrazone (2a). Equimolar amounts of 1-methyl-2-adamantanone (**1a**; 0.164 g, 1 mmol) and tosylhydrazine (0.186 g, 1 mmol) were dissolved in methanol (1 mL) and stirred for 15 h at room temperature. Water (20 mL) was then added, and the product was extracted with ether (3 × 50 mL). The combined extracts were washed with water (50 mL) and dried ($MgSO_4$). The solvent was removed in vacuo, and the crude product was recrystallized from pentane–ether (1:1) to give pure tosylhydrazone **2a**: 0.316 g (95%); ^{13}C NMR (C_6D_6) δ 169.3 (s, 1 C), 143.3 (s, 1 C), 136.7 (s, 1 C), 129.4 (d, 2 C), 128.9 (d, 2 C), 46.3 (t, 2 C), 39.8 (s, 1 C), 37.6 (t, 2 C), 35.6 (t, 1 C), 31.1 (d, 1 C), 28.2 (d, 2 C), 25.5 (q, 1 C), 21.1 (q, 1 C); ^{1}H NMR (C_6D_6) δ 8.50 (br s, 1 H), 8.15 and 6.92 (AB pattern of 4 H), 3.2 (br s, 1 H), 1.95 (s, 3 H), 1.83–1.20 (m, 12 H), 1.11 (s, 3 H); IR (KBr) 3200 (vs), 2920 (vs), 2850 (s), 1595 (s), 1455 (s), 1410 (s), 1160 (vs), 925 (s), 810 (s), 710 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.06; H, 7.23; N, 8.43. Found: C, 65.18; H, 7.40; N, 8.42.

1-Methyl-2-adamantanone Tosylhydrazone Lithium Salt (3a). *n*-Butyllithium (7.5 mL, 1.6 M solution in *n*-hexane) was slowly added via a syringe to a solution of 1-methyl-2-adamantanone tosylhydrazone (**2a**; 0.32 g, 9.6 mmol) in dry tetrahydrofuran (freshly distilled from CaH_2) stirred at 0 °C in a nitrogen atmosphere. A yellowish salt started to precipitate 30 min later. Stirring was continued for an additional hour at room temperature. The solvent was removed by evaporation, and the salt was dried for 3 h in vacuo (0.02 mmHg, 25 °C): IR (KBr) 3430 (br, m), 2900 (s), 1240 (s), 1130 (s), 1100 (s), 1080 (s), 1010 (m) cm^{-1}.

4-Chloro-4-protoadamantene (6). A solution of 4-protoadamantanone[11] (1.90 g, 12 mmol) and phosphorus pentachloride (2.4 g, 12 mmol) in carbon tetrachloride (150 mL) was stirred under reflux for 16 h. The reaction mixture was then cooled to room temperature and poured on ice. The layers were separated, and the aqueous one was extracted with dichloromethane (2 × 60 mL). The extracts were combined with the carbon tetrachloride solution, washed with water (3 × 60 mL), and dried ($MgSO_4$). Evaporation of the solvent gave 2.3 g of the crude product, which contained 80–86% of **6** (by GC; DEGS, 120 °C). Pure 4-chloro-4-protoadamantene (**6**; ≥97% by GC; 1.29 g, 61%) was obtained by column chromatography on silica gel with pentane as the eluent: ^{13}C NMR ($CDCl_3$) δ 141.1 (s, 1 C), 132.4 (d, 1 C), 45.2 (d, 1 C), 43.2 (t, 1 C), 41.2 (t, 1 C), 38.8 (t, 1 C), 38.7 (d, 1 C), 35.3 (d, 1 C), 33.2 (d, 1 C), 31.7 (t, 1 C). The ^{1}H NMR and IR spectral data are in complete agreement with those reported previously.[13b]

1-Chloro-2-(formyloxy)adamantane (7). A solution of 4-chloro-4-protoadamantene (**6**; 2.3 g, 14 mmol) in 98–100% formic acid (20 mL) was vigorously stirred in the presence of concentrated sulfuric acid (10 drops). The reaction was monitored by GC

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(30) This is in good agreement with the high regioselectivity of intramolecular carbene C–H insertions observed for various protoadamantylidenes[31] and some other geometrically rigid carbenes.[2]

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(DEGS, 120 °C), and after completion, the reaction mixture was poured on ice. The resulting mixture was extracted with dichloromethane (3 × 100 mL). The combined extracts were washed with water (120 mL), saturated sodium bicarbonate solution (120 mL), and water (120 mL) and then dried ($MgSO_4$). The solvent was removed, and the crude product was purified on a silica gel column. Elution with pentane–dichloromethane (1:1) gave pure (≥96% by GC; DEGS, 120 °C) 1-chloro-2-(formyloxy)adamantane (**7**): 1.52 g (52%); ^{13}C NMR ($CDCl_3$) δ 160.1 (d, 1 C), 78.9 (d, 1 C), 68.0 (s, 1 C), 47.0 (t, 1 C), 41.9 (t, 1 C), 35.4 (t, 1 C), 35.2 (t, 1 C), 35.1 (d, 1 C), 30.6 (d, 2 C), 29.8 (t, 1 C); ^1H NMR ($CDCl_3$) δ 8.0 (s, 1 H), 5.6 (br s, 1 H), 2.9–1.5 (m, 13 H); IR (film) 2910 (s), 1730 (vs), 1165 (s), 1030 (m), 990 (m) cm^{-1}; mass spectrum, *m/e* (relative intensity) 214 (M^+, 2), 169 (9), 134 (12), 126 (12), 92 (33), 91 (100), 79 (24). Anal. Calcd for $C_{11}H_{15}O_2Cl$: C, 61.68; H, 7.01; Cl, 16.35. Found: C, 61.84; H, 7.09; Cl, 16.27.

1-Chloro-2-hydroxyadamantane. A solution of 1-chloro-2-(formyloxy)adamantane (**7**; 2.0 g, 9 mmol) in dry ether (70 mL) was added dropwise to a suspension of $LiAlH_4$ (0.4 g, 11 mmol) in dry ether (10 mL) at 0 °C. The reaction mixture was stirred for 2 min at this temperature, and then the excess of $LiAlH_4$ was destroyed by a careful addition of wet ether followed by water. The product was extracted with dichloromethane (3 × 100 mL). The combined extracts were dried over $MgSO_4$. Evaporation of the solvent yielded 1.32 g (78%) of 1-chloro-2-hydroxyadamantane (98% pure by GC; DEGS, 120 °C): ^{13}C NMR ($CDCl_3$) δ 78.0 (d, 1 C), 74.6 (s, 1 C), 46.4 (t, 1 C), 40.9 (t, 1 C), 36.0 (d, 1 C), 35.7 (t, 2 C), 31.3 (d, 1 C), 31.2 (d, 1 C), 29.1 (t, 1 C); ^1H NMR ($CDCl_3$) δ 3.75 (br s, 1 H), 2.7 (s, 1 H), 2.3–1.3 (m, 13 H); IR (KBr) 3450 (br, s), 2910 (s), 2860 (m), 1455 (s), 1055 (m), 1025 (s), 840 (s), 715 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 188 (M^+ + 2, 6), 186 (M^+, 18), 170 (33), 168 (100), 151 (41), 133 (42), 91 (72), 79 (82), 77 (45). Anal. Calcd for $C_{10}H_{15}OCl$: C, 64.52; H, 8.06; Cl, 18.81. Found: C, 64.39; H, 8.30; Cl, 18.43.

1-Chloro-2-adamantanone (1b). To a solution of 1-chloro-2-hydroxyadamantane (1.0 g, 5.3 mmol) in acetone (50 mL) stirred at room temperature was added Jones reagent dropwise until a permanent red color appeared. The reaction mixture was stirred for an additional hour, and 2-propanol (2 mL) was added to reduce the excess of chromic oxide. The resulting solution was diluted with water (50 mL) and extracted with chloroform (3 × 50 mL). The organic layer was washed with saturated sodium bicarbonate solution (100 mL) and water (2 × 50 mL) and then dried ($MgSO_4$). Evaporation of the solvent yielded 0.93 g (95%) of pure (≥98% by GC; DEGS, 160 °C; QF, 150 °C,) 1-chloro-2-adamantanone (**1b**): ^{13}C NMR ($CDCl_3$) δ 206.8 (s, 1 C), 74.0 (s, 1 C), 49.4 (t, 2 C), 47.9 (d, 1 C), 38.2 (t, 2 C), 34.4 (t, 1 C), 30.4 (d, 2 C); ^1H NMR ($CDCl_3$) δ 2.9 (br s, 1 H), 2.5–1.7 (m, 12 H); IR (KBr) 2930 (s), 1750 (s), 1735 (s), 1055 (m) 1036 (m), 765 (s), 640 (m) cm^{-1}; mass spectrum, *m/e* (relative intensity) 186 (M^+ + 2, 51), 184 (M^+, 100), 149 (50), 121 (79), 103 (76), 91 (41), 80 (85), 79 (87). Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.22; H, 7.06; Cl, 19.02. Found: C, 64.89; H, 6.95; Cl, 18.78.

1-Chloro-2-adamantanone tosylhydrazone (2b) was prepared in 89% yield from ketone **1b** by the procedure described for **2a**: ^{13}C NMR ($CDCl_3$) δ 163.0 (s, 1 C), 143.6 (s, 1 C), 134.7 (s, 1 C), 129.0 (d, 2 C), 128.1 (d, 2 C), 68.5 (s, 1 C), 49.2 (t, 2 C), 36.2 (t, 2 C), 34.1 (t, 1 C), 33.2 (d, 1 C), 30.1 (d, 2 C), 21.4 (q, 1 C); ^1H NMR ($CDCl_3$) δ 7.9 (br s, 1 H), 7.8 and 7.2 (AB pattern of 4 H), 3.16 (br s, 1 H), 2.4 (s, 3 H), 2.15 (br s, 6 H), 1.80 (br s, 6 H); IR (KBr) 3260 (s), 3230 (s), 2930 (vs), 2860 (s), 1600 (m), 1450 (m), 1350 (s), 1335 (s), 1335 (s), 1180 (vs), 910 (m), 810 (m), 710 (s), 690 (s) cm^{-1}.

1-Chloro-2-adamantanone Tosylhydrazone Sodium Salt (3b). Sodium hydride (50% suspension in mineral oil, 0.024 g, 0.5 mmol) was added in five portions to a solution of 1-chloro-2-adamantanone tosylhydrazone (**2b**; 0.176 g, 0.5 mmol) in dry tetrahydrofuran (5 mL) stirred at room temperature. The resulting thick suspension was stirred for additional 2 h, the solvent was then removed by evaporation, and the salt was dried for 3 h in vacuo (0.02 mmHg, 25 °C): IR (KBr) 3500 (br, m), 2920 (s), 2850 (m), 1450 (m), 1235 (s), 1120 (s), 1090 (m), 1070 (m), 1025 (s), 930 (m), 810 (m), 710 (s), 655 (s) cm^{-1}.

5-Methyl-2-adamantanone (1c) was obtained in 8% overall yield by oxidation of 1-methyladamantane[12] (3.08 g, 20 mmol) with concentrated sulfuric acid by following the reported procedure.[14] Ketone **1c** (0.26 g; ≥97% pure by GC; DEGS, 135 °C) was isolated by three successive chromatographies on a 10% charcoal–silica gel column with pentane as the eluent: ^{13}C NMR ($CDCl_3$) δ 218.6 (s, 1C), 46.6 (d, 2 C), 45.6 (t, 2 C), 43.3 (t, 1 C), 38.6 (t, 2 C), 30.0 (s, 1C), 29.2 (q, 1 C), 28.1 (d, 1 C). The ^1H NMR, IR, and mass spectra are in complete agreement with those reported previously.[14]

5-Methyl-2-adamantanone tosylhydrazone (2c) was prepared in 96% yield from ketone **1c** by the procedure described for **2a**: ^{13}C NMR (C_6D_6) δ 170.5 (s, 1 C), 143.7 (s, 1 C), 135.3 (s, 1 C), 129.3 (d, 2 C), 127.9 (d, 2 C), 45.3 (t, 1 C), 43.9 (t, 1 C), 43.1 (t, 1 C), 39.4 (d, 1 C), 38.2 (t, 1 C), 36.9 (t, 1 C), 31.4 (d, 1 C), 29.9 (s, 1 C), 29.5 (q, 1 C), 28.1 (d, 1 C), 21.5 (q, 1 C); ^1H NMR ($CDCl_3$) δ 7.8 (br s, 1 H), 7.7 and 7.3 (AB pattern for 4 H), 3.0 (br s, 1 H), 2.6 (br s, 1 H), 2.4 (s, 3 H), 1.9 (br s, 1 H), 1.8–1.3 (m, 10 H), 0.8 (s, 3 H); IR (KBr) 3220 (vs), 2920 (s), 1640 (m), 1445 (m), 1320 (s), 1305 (s), 1165 (vs), 1155 (vs), 1090 (m), 1005 (m), 920 (m), 820 (s), 740 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.06; H, 7.23; N, 8.43. Found: C, 64.81; H, 7.47; N, 8.64.

5-Methyl-2-adamantanone tosylhydrazone sodium salt (3c) was obtained from tosylhydrazone **2c** using the procedure described for **3b**: IR (KBr) 3450 (br, m), 2920 (s), 2840 (m), 1450 (m) 1240 (s), 1125 (s), 1100 (m), 1080 (m), 820 (m), 660 (s) cm^{-1}.

5-Chloro-2-adamantanone (1d). A solution of 5-hydroxy-2-adamantanone (1.66 g, 10 mmol; prepared in 80% yield by oxidation of 2-adamantanone[30] with fuming HNO_3[15]) in thionyl chloride (8 mL) was stirred for 3 h at 78–80 °C, cooled to room temperature, and evaporated to dryness. Dichloromethane (150 mL) was added, and the resulting solution was washed with water (100 mL), saturated sodium bicarbonate solution (100 mL) and water (100 mL) and then dried over calcium chloride. The crude product was passed through a short silica gel column with pentane–ether (2:1) as the eluent to yield 1.43 g (78%) of ketone **1d** (≥96% pure by GC; DEGS, 160 °C): ^{13}C NMR ($CDCl_3$) δ 214.5 (s, 1 C), 64.5 (s, 1 C), 48.0 (d, 2 C), 47.4 (t, 2 C), 46.3 (d, 1 C), 37.5 (d, 1 C); ^1H NMR ($CDCl_3$) δ 2.6 (br s, 3 H), 2.4 (br s, 6 H), 2.06 (br s, 4 H); IR (KBr) 2940 (s), 2860 (m), 1730 (s), 1450 (m), 1060 (m), 1025 (m), 827 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 186 (M^+ + 2, 30), 184 (M^+, 98), 149 (9), 91 (21), 80 (33), 79 (100), 77 (13).

5-Chloro-2-adamantanone tosylhydrazone (2d) was prepared in 94% yield from ketone **1d** by the procedure described for **2a**: ^{13}C NMR ($CDCl_3$) δ 165.7 (s, 1 C), 143.8 (s, 1 C), 135.0 (s, 1 C), 129.5 (d, 2 C), 127.8 (d, 2 C), 65.3 (s, 1 C), 47.6 (t, 1 C), 46.2 (t, 2 C), 41.2 (d, 1 C), 37.0 (t, 1 C), 35.7 (t, 1 C), 33.2 (d, 1 C), 30.7 (d, 1 C), 21.6 (q, 1 C); ^1H NMR ($CDCl_3$) δ 8.3 (br s, 1 H), 7.9 and 7.3 (AB pattern for 4 H), 3.2 (br s, 1 H), 2.7 (br s, 1 H), 2.4 (s, 3 H), 2.3–1.6 (m, 11 H); IR (KBr) 3210 (vs), 2920 (s), 2910 (s), 2860 (m), 1165 (s), 1030 (s), 920 (s), 830 (s), 735 (s), 670 (vs) cm^{-1}. Anal. Calcd for $C_{17}H_{21}N_2O_2SCl$: C, 57.95; H, 5.96; N, 7.95; Cl, 9.09. Found: C, 58.22; H, 5.99; N, 8.18; Cl, 9.36.

5-Chloro-2-adamantanone tosylhydrazone sodium salt (3d) was obtained from tosylhydrazone **2d** by using the procedure described for **3b**: IR (KBr) 3450 (br, m), 2930 (s), 2850 (m), 1450 (m), 1230 (s), 1130 (vs), 1090 (vs), 1080 (m), 1030 (s), 825 (m), 805 (m), 745 (m), 670 (m), 655 (s) cm^{-1}.

Pyrolyses of the Tosylhydrazone Alkali Salts 3a–d. Each of the four salts was prepared and pyrolyzed at least three times. The same flask was used for preparation, drying, and pyrolysis of the salts. In a typical experiment, the reaction flask containing 1.5 mmol of a dry salt was connected to a vacuum pump via a trap, evacuated at 0.05 mmHg for 30 min, and then immersed into an oil bath at 170 °C. The temperature of the bath was rapidly risen to 180 °C. The products were collected in the trap which was cooled with liquid nitrogen. The products of the methyl tosylhydrazone salts, **3a** and **3c**, were obtained in 15–18% yields, while the chloro tosylhydrazone salts, **3b** and **3d**, yielded 26–28% products.

Each product mixture was analyzed by quantitative ^{13}C NMR and four to eight times by GC (capillary Carbowax 20M column, 60 °C, for the products of **3a** and **3c**; DEGS, 120 °C, for the products of **3b** and **3d**). The product mixtures of **3a** and **3c** were purified, prior to being subjected to the ^{13}C NMR, ^1H NMR, IR, and mass spectral analyses, on a short 10% charcoal–silica gel column with pentane as the eluent. The GC, ^{13}C NMR, and ^1H NMR analyses of the purified mixtures showed no change in the

product ratios and indicated the presence of 4–5% of 1-methyladamantane. The products of **3b** and **3d** were separated by three successive chromatographies on a neutral alumina (activity II/III) column with pentane as the eluent.

The products were identified by ^{13}C NMR (see Table I), ^1H NMR, IR, and mass spectra.

For the mixture of **3-methyl-2,4-didehydroadamantane (8a)** and **1-methyl-2,4-didehydroadamantane (9a)** obtained from **4a**: ^1H NMR (C_6D_6) δ 2.3–1.2 (complex m, maximums at δ 2.2, 1.7, 1.3), 1.11 (s, CH_3), and 0.95 (s, CH_3); IR (film) 3040 (m–w), 2930 (s), 2840 (s), 1450 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 148 (M^+, 37), 133 (11), 119 (13), 93 (51), 92 (60), 91 (92), 79 (100), 77 (43), 70 (40). Anal. Calcd for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 88.99; H, 10.83.

For the mixture of **1-methyl-2,4-didehydroadamantane (9a)** and **7-methyl-2,4-didehydroadamantane (10a)**: ^1H NMR (C_6D_6) δ 2.4–1.0 [complex m, maximums at δ 2.26, 1.52, 1.12, 1.11 (s, CH_3), and 0.75 (s, CH_3)]; IR (film) 3030 (w–m), 2990 (w), 2920 (s), 2840 (s), 1450 (m) cm^{-1}; mass spectrum, *m/e* (relative intensity) 148 (M^+, 100), 133 (48), 106 (78), 105 (67), 93 (77), 91 (94), 79 (95), 78 (30), 77 (41). Anal. Calcd for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 89.12; H, 10.95.

1-Chloro-2,4-didehydroadamantane (9b): ^1H NMR ($CDCl_3$) δ 2.8–0.7 (complex m, maximums at δ 2.7, 2.0, 1.9, 1.8, 1.3, and 1.2); IR (film) 3040 (m), 2930 (s), 2860 (m), 1460 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+ + 2, 11), 168 (M^+, 31), 133 (40), 126 (19), 93 (35), 92 (55), 91 (100), 81 (31), 79 (56). Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.43; H, 7.74; Cl, 20.83. Found: C, 71.47; H, 7.48; Cl, 20.54.

3-Chloro-2,4-didehydroadamantane (8b): ^1H NMR ($CDCl_3$) δ 2.6–0.7 (complex m, maximums at δ 2.4, 2.2, 2.0, 1.9, 1.4, and 1.3); IR (film) 3030 (m), 2920 (s), 2850 (s), 1450 (w), 720 (w) cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+ + 2, 10), 168 (M^+, 32), 133 (39), 126 (32), 113 (37), 92 (25), 91 (100), 81 (47), 79 (49). Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.43; H, 7.74; Cl, 20.83. Found: C, 71.41; H, 7.69; Cl, 20.76.

7-Chloro-2,4-didehydroadamantane (10b): ^1H NMR ($CDCl_3$) δ 2.7–1.3 (complex m, maximums at δ 2.5, 2.2, 1.9, 1.8, and 1.5); IR (KBr) 3030 (m), 2940 (s), 2860 (s), 1450 (w), 1440 (w), 1315 (w), 1025 (s), 850 (s), 795 (s), 740 (m), 630 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 170 (M^+ + 2, 4), 168 (M^+, 13), 133 (11), 126 (11), 92 (17), 91 (83), 79 (100), 78 (70), 77 (36). Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.43; H, 7.74; Cl, 20.83. Found: C, 71.33; H, 7.65; Cl, 20.53.

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Registry No. 1a, 26832-19-9; **1b**, 81315-72-2; **1c**, 21365-84-4; **1d**, 20098-17-3; **2a**, 81315-73-3; **2b**, 81315-74-4; **2c**, 81315-75-5; **2d**, 81315-76-6; **3a**, 81315-77-7; **3b**, 81315-78-8; **3c**, 81315-79-9; **3d**, 81315-80-2; **4a**, 81315-81-3; **4b**, 81315-82-4; **4c**, 81315-83-5; **4d**, 81315-84-6; **5**, 27567-85-7; **6**, 28996-05-6; **7**, 81315-85-7; **8a**, 81315-86-8; **8b**, 81315-87-9; **9a**, 81315-88-0; **9b**, 81315-89-1; **10a**, 81315-90-4; **10b**, 81315-91-5; 1-chloro-2-hydroxyadamantane, 81315-92-6; 1-methyladamantane, 768-91-2; 5-hydroxy-2-adamantanone, 20098-14-0.

Optically Active Amines. 30.[1a] Application of the Salicylidenimino Chirality Rule to Aliphatic and Alicyclic Amines[1b]

Howard E. Smith,*[2a] Clinton A. Taylor, Jr.,[2a,3] Antony F. McDonagh,[2a] and Fu-Ming Chen[2b]

Departments of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Tennessee State University, Nashville, Tennessee 37203, and the Center for Population Research and Studies in Reproductive Biology,[4] Vanderbilt University, Nashville, Tennessee 37235

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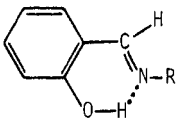
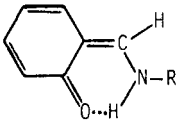
The salicylidenimino chirality rule can be used to correlate the sign of the observed Cotton effects near 315 and 255 nm in the circular dichroism spectra of the *N*-salicylidene derivatives of aliphatic and alicyclic amines with their absolute configurations. The rule is based on the model that the Cotton effects originate from interaction of the respective transition moments of the hydrogen-bonded salicylidenimino chromophore with bond transition moments in the rest of the molecule. Carbon–carbon and carbon–oxygen bonds vicinal and homovicinal to the salicylidenimino attachment bond are the dominant contributors to the Cotton effects, and the sign of the Cotton effects depends on the algebraic sum of these contributions. Since the polarizability of a carbon–oxygen bond is smaller than that of a carbon–carbon bond, the contribution of a vicinal or homovicinal carbon–oxygen bond is less than that of a corresponding carbon–carbon bond. The sign of a particular contribution usually can be determined by the chirality that the bond has with the attachment bond of the salicyclidenimino group, a positive contribution for positive chirality (right-handed screw) and a negative contribution for negative chirality (left-handed screw).

The isotropic electronic absorption (EA) spectra of the *N*-salicylidene derivatives of chiral primary amines in hexane exhibit characteristic absorption bands at about 315 (log ϵ_{max} 3.7), 255 (4.1–4.2), and 215 nm (4.4–4.5), designated as bands I–III, respectively,[5] which were assigned to the $\pi \rightarrow \pi^*$ transitions of the intramolecularly hydrogen-bonded salicylidenimino (SI) chromophore (**1**).[6]



1



2

In polar solvents, a broad band at about 400 nm (log ϵ_{max} 1.3–1.9 in dioxane[7] and 3.1–3.4 in methanol[5] and ethanol[7]) and a shoulder near 280 nm (log ϵ_{max} 3.5–3.7 in ethanol[7])

(1) (a) Part 29: Smith, H. E.; Chen, F.-M. *J. Org. Chem.* **1981**, *46*, 185–187. (b) Some of this work was taken from the Ph.D. Thesis of A.F.M., Vanderbilt University, Jan 1967.

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(4) Supported by National Institutes of Health Grant HD-05797.

(5) Smith, H. E.; Burrows, E. P.; Massey, E. H.; Chen, F.-M. *J. Org. Chem.* **1975**, *40*, 2897–2901.

(6) Alexander, P. W.; Sleet, R. J. *Aust. J. Chem.* **1970**, *23*, 1183–1190.

(7) Ripperger, H.; Schreiber, K.; Snatzke, G.; Ponsold, K. *Tetrahedron* **1969**, *25*, 827–836.

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