Rearrangements of Oxahomoadamantane Derivatives in Acidic Media

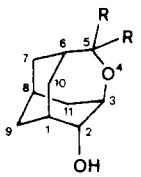
Helmut Duddeck,* Volker Wiskamp, and Doris Rosenbaum

Ruhr-Universität Bochum, Abteilung für Chemie, D-4630 Bochum 1, Federal Republic of Germany

Received March 25, 1981

2-*anti*-Hydroxy-4-oxa-5-homoadamantane derivatives **1a–c** in acidic media can undergo rearrangement reactions which strongly depend on the substituents R at C^5. Whereas the parent alcohol **1b** (R = H) can only be transformed into derivatives of the same isomeric series (e.g., the chloride **9b**), the dimethyl analogue **1a** (R = CH_3) is able to rearrange to oxaadamantanes (**6**, **8**, and **10**). The lactone **1c**, however, gives the diketone **17**. In all instances, epoxonium ions **2a–c** are supposed to be intermediates. Treated with hydrobromic or hydroiodic acid, **1a–c** are reduced to form adamantane derivatives.

During the course of our ^{13}C NMR investigations of diamondoid compounds we synthesized a series of 2-*anti*-hydroxy-4-oxa-5-homoadamantanes (**1a–c**) according



	R / R
1a	CH_3 / CH_3
1b	H / H
1c	O

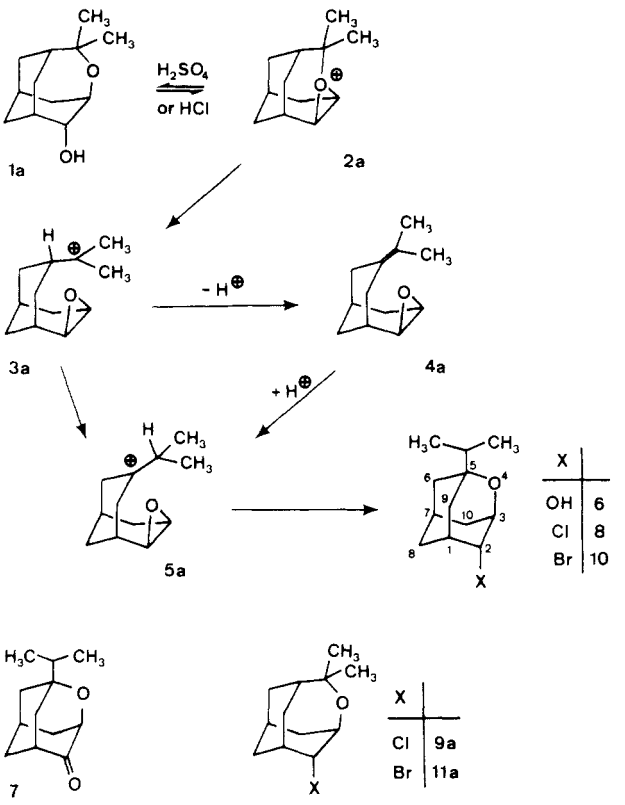
to known procedures.[1] Our attempts to convert these alcohols into isomers, corresponding halides, etc. afforded unexpected and interesting rearrangement reactions which we report in this paper.

Results and Discussion

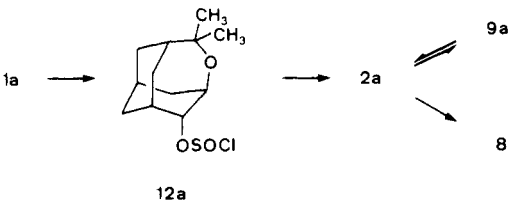
Rearrangements to Oxaadamantanes. When treated with 60% sulfuric acid the alcohol **1a** undergoes an unexpected rearrangement to form 4-*anti*-hydroxy-1-isopropyl-2-oxaadamantane (**6**, Scheme I). The mechanism of this reaction may be rationalized as follows. In the first step the hydroxy group is protonated, and water elimination leads to the formation of the epoxonium ion **2a**. Ring opening gives the carbenium ion **3a** which is converted to **5a**. Anti attack of water with epoxide opening finally leads to the *anti*-alcohol **6**. The conversion of **3a** to **5a** can be achieved either by deprotonation to the olefin **4a** with subsequent reprotonation or by a hydride shift. An experiment using deuterated sulfuric acid shows that both pathways are followed, the second being slightly favored. The intermediate formation of **4a** is revealed by deuterium incorporation at the methine carbon of the isopropyl group in the final product **6**. Comparison of the M^+ and $M^+ + 1$ peaks in the mass spectrum of the isolated compound **6** indicated that only 40% of the molecules contained one deuterium atom.

The structure of **6** was determined by its ^{13}C NMR spectral data, (Table I). The ^{13}C chemical shifts of all isomeric isopropyloxaadamantanols can be calculated by adding substituent chemical shift (SCS) effects of hydroxy and isopropyl groups to the chemical shifts of the appropriate carbons in the conceived molecule (see Table I); the SCS are obtained by subtracting the chemical shifts of the unsubstituted adamantane from those of 2-hydroxy- or 1-isopropyladamantane, respectively. Table I shows that the calculated and experimental ^{13}C chemical shifts are in excellent accordance, if the isopropyl and the hydroxy

Scheme I



Scheme II



12a

group are arranged in the 1- and 4-*anti*-positions, respectively, as depicted in formula **6**. The discrepancies at C^3 and C^4 are nonadditivity effects of SCS of the two oxygen functionalities. They fit nicely the expectations based on reports of other vicinally disubstituted compounds.[5] Thus, these good agreements rule out all other isomers. Furthermore, the signal assignments in the

(1) D. L. Goff and R. K. Murray, Jr., *J. Org. Chem.*, **43**, 3179 (1978).
(2) W. Fischer and C. A. Grob, *Helv. Chim. Acta*, **61**, 1588 (1978).
(3) H. Duddeck and P. Wolff, *Org. Magn. Reson.*, 8, 593 (1976).
(4) H. Duddeck, *Org. Magn. Reson.*, 7, 151 (1975).
(5) C. L. Antwerp, H. Eggert, G. D. Meakins, J. O. Miners, and C. Djerassi, *J. Org. Chem.*, **42**, 789 (1977); J. R. Bull and A. A. Chalmers, *S. Afr. J. Chem.*, **30**, 105 (1977); G. Engelhardt and D. Zeigan, *J. Prakt. Chem.*, **320**, 377 (1978); H.-J. Schneider, G. Becker, W. Freitag, and V. Hoppen, *J. Chem. Res., Synop.*, **1979**, 14; E. Kleinpeter, G. Haufe, and R. Borsdorf, *J. Prakt. Chem.*, **322**, 125 (1980).

0022-3263/81/1946-5332$01.25/0

Table I. Calculated and Experimental ^{13}C Chemical Shifts of 4-*anti*-Hydroxy-1-isopropyl-2-oxaadamantane (6)[a] and Substituent Chemical Shifts

	SCS (*i*-Pr)[b]	2-oxaada-mantane[c]	SCS (OH)[d]	6	
				calcd	exptl
C^1	+5.9	67.8	−1.2	72.5	73.5
C^3	+0.5	67.8	+6.2	74.5	71.4
C^4	−0.2	36.1	+36.9	72.8	70.6
C^5	+0.5	26.5	+6.2	33.2	33.6
C^6	−0.2	35.8	−6.6	29.0	29.6[e]
C^7	+0.5	26.5	−0.7	26.3	26.3
C^8	+1.6	36.1	0.0	37.7	36.6
C^9	+1.6	36.1	−1.1	36.6	36.5
C^{10}	−0.2	36.1	−6.6	29.3	29.4[e]
i-Pr	+30.4 (CH)				37.4 (CH)
	+16.3 (CH_3)				16.6 (CH_3)

[a] In parts per million relative to internal tetramethylsilane with deuteriochloroform as the solvent. [b] Substituent chemical shift (SCS) effects of the isopropyl group in 1-isopropyladamantane (see text), arranged according to the position of this group in **6**. 1-Isopropyladamantane was obtained by palladium-catalyzed hydrogenation of 1-isopropenyladamantane which was prepared from 1-adamantane carboxylic acid according to ref 2. [c] Taken from ref 3 and arranged according to the position of the oxygen atom in **6**. [d] Substituent effects of the hydroxy group in 2-hydroxyadamantane,[4] arranged according to the position of the hydroxy group in **6**. [e] May be interchanged.

spectrum of **6** are confirmed by ^{13}C NMR measurements in the presence of the lanthanide shift reagent Yb(fod)$_3$.[6] Jones oxidation[7] of **6** gave the ketone **7** in 63% yield, the ^{13}C NMR data of which were also reported earlier.[6]

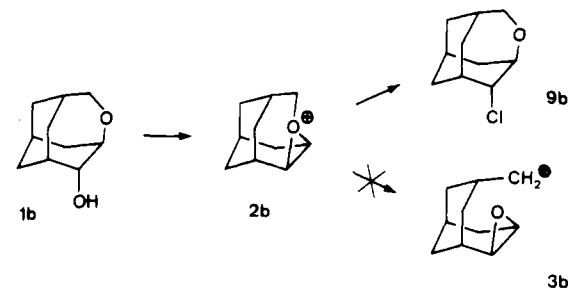
Reaction of **1a** in hydrochloric acid afforded a 1:1 mixture of **6** and **8**. Apparently there is competition between H_2O and Cl^- in the attack of carbenium ion **5a**. This is similar to what was observed in the reaction of 4-oxa-5-homoadamantan-5-one[8,9] with concentrated hydrochloric acid to form 4-substituted adamantanones.[10]

Refluxing **1a** in freshly distilled thionyl chloride gave 2-*anti*-chloro-5,5-dimethyl-4-oxa-5-homoadamantane (**9a**) as the sole product. If, however, this reaction is carried out in an excess of pyridine, the isomeric *syn*-chloride is expected. In fact, the only product observed is the *anti*-chloride again. This indicates that these reactions are not following the well-known nucleophilic substitution mechanisms. Instead, **12a** is converted into the epoxonium ion **2a** (Scheme II) which can form only the *anti*-chloride **9a** because of stereochemical reasons. Thionyl chloride which was not purified immediately prior to use gave the rearrangement product **8** in a side reaction (10–20%) under the same conditions (2 h at reflux). Probably the rearrangement is accelerated by hydrogen chloride present in unpurified thionyl chloride. Extending the reaction time to 72 h changes the **8**/**9a** ratio entirely in favor of **8**. This suggests that there is a **2a** ⇌ **9a** equilibrium, while the rearrangement is irreversible. Accordingly, **9a** is also converted to **8** under these conditions.

In the reaction of **1a** with thionyl bromide only 4-*anti*-bromo-1-isopropyl-2-oxaadamantane (**10**) is formed. Exposure of **1a** to 48% hydrobromic acid or 57% hydriodic acid did not afford the bromides **10** and/or **11a** and the corresponding iodides, respectively, but reduction products which are discussed below.

Treatment of **1b** with thionyl chloride in pyridine yielded 2-*anti*-chloro-4-oxa-5-homoadamantane (**9b**, Scheme III), presumably again via an epoxonium ion (**2b**); no syn isomer was observed. Experiments designed to achieve rearrangements analogous to those of **1a** failed,

Scheme III



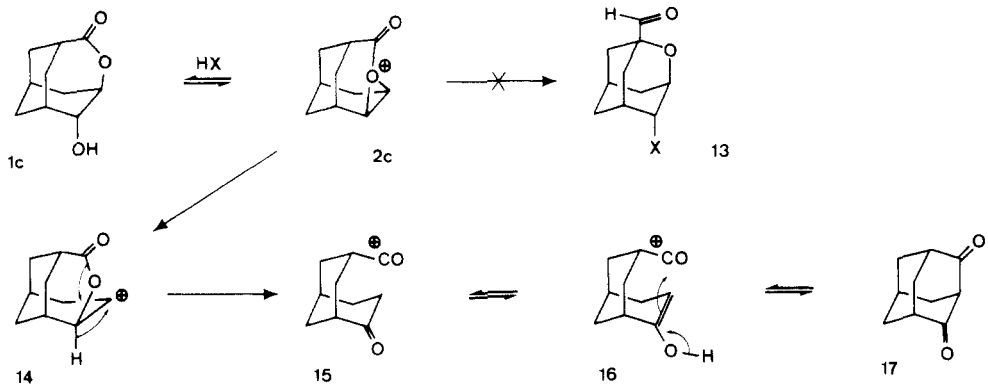
since that would imply the formation of the primary carbenium ion **3b**. This finding nicely corroborates the mechanisms depicted in Scheme I.

Epoxonium–Ketone Rearrangement. In acidic media **1c** undergoes a rearrangement completely different from that in the case of **1a** (Scheme IV). There is no formation of formyloxaadamantane derivative **13**. In contrast to **2a** and **2b**, the epoxonium ion **2c** is able to undergo an epoxonium–ketone rearrangement to **15** via an intermediate carbenium ion, **14**, because of the electron-withdrawing ability of the carbonyl group. Tautomerization of **15** to **16** and subsequent loss of a proton finally leads to the diketone **17** which is identical with an authentic sample.[8,11] This reaction is analogous to the reported Lewis acid catalyzed epoxide–ketone rearrangement.[12,13] To the best of our knowledge this is the first instance of a carbonyl group adopting the role of a Lewis acid in this reaction.[14]

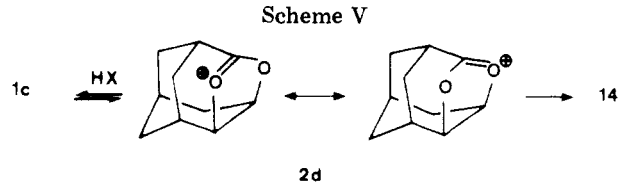
There is an alternate intermediate (**2d**) conceivable in this reaction (Scheme V). Here the carbonyl oxygen acts as a nucleophile. As can easily be seen from Dreiding models, however, in contrast to **2c** the intermediate **2d** is highly strained, and its formation requires a severe distortion of the precursor **1c**. Since **2c** is closely related to the intermediates **2a** and **2b** and because of the analogy to Lewis acid catalyzed epoxide–ketone rearrange-

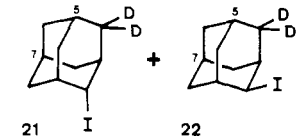
(6) H. Duddeck and V. Wiskamp, *Org. Magn. Reson.*, **15**, 361 (1981).
(7) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).
(8) D. Faulkner and M. A. McKervey, *J. Chem. Soc. C*, 3906 (1971); and references therein.
(9) L. Vodicka, J. Hlavaty, and S. Landa, *Collect. Czech. Chem. Commun.*, **38**, 3302 (1973).
(10) H. Duddeck and P. Wolff, *Org. Magn. Reson.*, **9**, 528 (1977).
(11) M. A. McKervey, D. Faulkner, and H. Hamill, *Tetrahedron Lett.*, 1971 (1970).
(12) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, *Aust. J. Chem.*, **23**, 839, 2077 (1970).
(13) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, *J. Am. Chem. Soc.*, **92**, 2574 (1970).
(14) For a survey of other catalysts see: A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings", Vol. 1, Part 1, A. Weissberger, Ed.; Wiley-Interscience, New York, 1964; L. A. Paquette, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **5**, 127 (1973).

Scheme IV



Scheme V





ments,[12-14] we believe that **2c** should be preferred as intermediate in this reaction.

Reductions. Treatment of the 2-*anti*-hydroxy-4-oxa-5-homoadamantanes **1a–c** with hydriodic acid (57%) gives rise to reduction reactions, the mechanisms of which can be rationalized as shown in Scheme VI. In the first step the *anti*-iodo derivatives **18** are formed via the epoxonium ion **2** (see above). The compounds **18**, however, cannot be isolated, since they are prone to HI reduction, producing the olefinic alcohols **19a** and **19b** or the acid **19c**, respectively. Attack of an iodide anion and ring closure gives the iodoadamantane derivatives **21–25**. Treatment of separately prepared **19a** and **19b**[1] under identical conditions leads to the same products.

At this stage the question arises as to whether the iodine incorporation is stereoselective or not. In the case of **1b** (R = H) the two conceivable products (anti or syn attack of the iodide with respect to the substituent(s) R) are identical. In order to label the adamantane moiety, we synthesized the 5,5-dideuterio derivative **1b**[1] (R = D). The composition of the resulting epimeric mixture of **21** and **22** can now be determined by inspecting the ^{13}C NMR signals of the carbons in positions with respect to the iodine (C^5 and C^7) (Figure 1). It is known[15] that the signal of the *δ-anti*-carbon in 2-iodoadamantane appears at higher field than that of the *δ*-syn atom. Thus, the two high-field signals in the spectrum of the mixture of the deuterated **21** and **22** (Figure 1) correspond to C^7 (**22**) and C^5 (**21**) and those at lower field to C^7 (**21**) and C^5 (**22**). It is interesting to note that the C^5 signals experience rather large isotopic upfield shifts of 0.20 ppm due to the deuterium atoms in the *β*-position; the slight line broadening is caused by deuterium–carbon coupling.

As can be seen from the spectral data, the intensities (peak areas) are approximately equal. Thus, the sample consists of a 1:1 mixture;[16] there is no stereoselectivity. It cannot be decided, however, whether the iodide attack itself is nonstereoselective or whether an originally existing stereoselectivity is masked by a subsequent epimerization. Such an epimerization is possible under the applied conditions: if **1b** is exposed to 48% hydrobromic acid, 2-bromoadamantane is formed in an analogous reaction. Thus, if 2-bromoadamantane is treated with hydriodic acid, 2-iodoadamantane should be synthesized and, conversely, 2-bromoadamantane, if 2-iodoadamantane is refluxed in hydrobromic acid. In fact, mixtures of both compounds are isolated in either experiment.

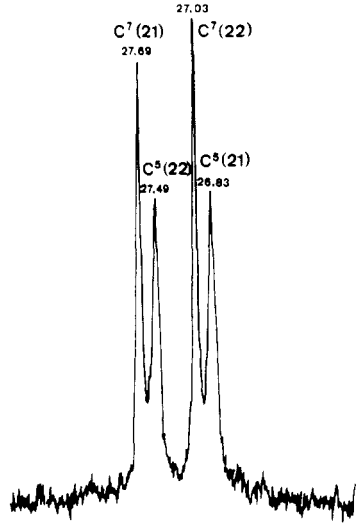


Figure 1. C^5 and C^7 NMR signals of a mixture of the two epimeric 2-iodo-4,4-dideuterioadamantanes **21** and **22**.

In the reaction of **1a** (R = CH_3) with hydriodic acid only one product (**23**) is found. Evidently, the axial methyl group directs the halide ion into the anti position exclusively, because **23** is the thermodynamically more stable isomer. With hydrobromic acid, the corresponding 2-*anti*-4,4-dimethyladamantane is obtained.

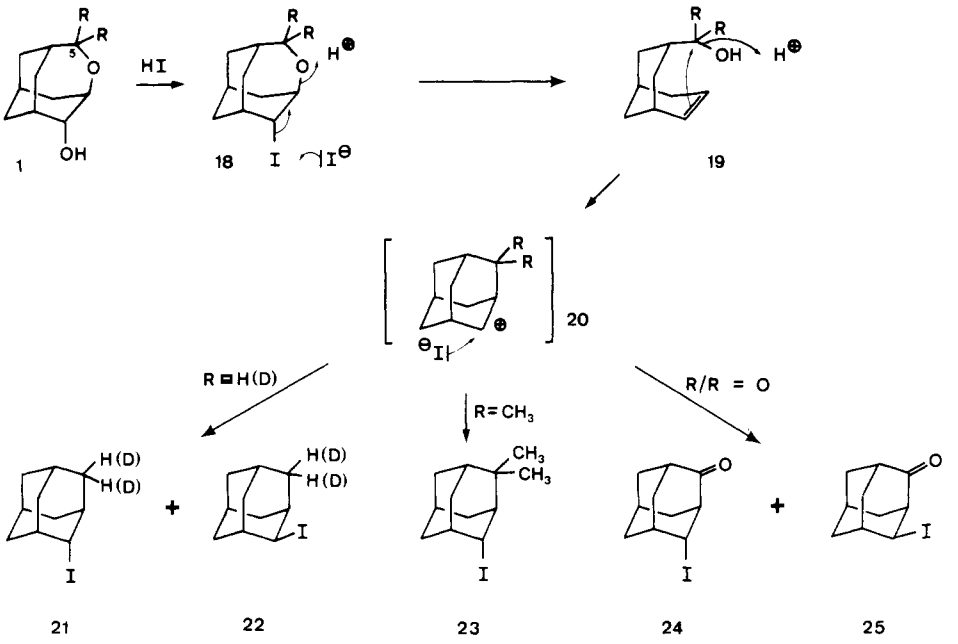
A similar reaction was described by McKervey et al.,[17] who prepared an epimeric mixture of 4,4-dimethyladamantanols by reaction of **19a** (R = CH_3) with formic acid. The lactone **1c** afforded the *syn*-iodoadamantanone **25** as the sole product, if it is refluxed with hydriodic acid overnight. When it is exposed to refluxing hydriodic acid only for 45 min, 15% of the anti isomer **24** is also obtained. In hydrobromic acid, however, the epoxonium–ketone rearrangement (see above) is much faster than the reduction,

(15) R. Gerhards, W. Dietrich, G. Bergmann, and H. Duddeck, *J. Magn. Reson.*, **36**, 189 (1979).

(16) This is only valid if the longitudinal relaxation times T_1 of the carbons concerned are equal. To our experience, however, this is an admissible assumption.

(17) F. Blaney, D. Faulkner, M. A. McKervey, and G. Step, *J. Chem. Soc., Perkin Trans. 1*, 2697 (1972).

Scheme VI



and only the diketone **17** is formed.

Experimental Section

Melting points were determined in sealed capillary tubes by using a Büchi-Tottoli melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer, ^{1}H NMR spectra were obtained on Varian T-60 and A-60 or Bruker HFX-90 spectrometers and ^{13}C NMR spectra on a Bruker WH-90 spectrometer. For the NMR spectra the solvent was deuterated chloroform, and the chemical shifts are referenced to internal tetramethylsilane. Mass spectra were recorded on Varian CH-5 and 731 spectrometers. The elemental analyses were performed by Fa. Ilse Beetz, Mikroanalytisches Laboratorium.

All compounds were purified by column chromatography with silica gel and various ligroin/acetone mixtures as eluants and were >98% pure according to GLC analysis. Compounds already known in literature (**1a**,[1] **1b**,[1] **17**,[8,11] **19b**,[18] **21**,[10] **24**,[10] and **25**[10]) were identified by comparing their spectra. In some instances authentic samples were available for comparison by thin-layer chromatography. All reported yields refer to isolated samples after purification. They are not optimized and are sometimes low due to the high volatility of many of the compounds.

2-*anti*-Hydroxy-4-oxa-5-homoadamatan-5-one (1c). *endo*-Bicyclo[3.3.1]non-6-ene-3-carboxylic acid[8] (5.0 g, 30 mmol) and *m*-chloroperbenzoic acid (9.0 g, 52 mmol) were dissolved in 400 mL of methylene chloride and refluxed overnight. The solution was washed successively with sodium bisulfite, sodium bicarbonate, and water. After the mixture was dried over anhydrous magnesium sulfate, the solvent of the organic layer was evaporated. Purification of the crude product by column chromatography gave 3.8 g (70% yield) of **1c** as a white solid: mp 299–300 °C; IR ($CHCl_3$) 3600–3100 (OH), 2925, 1725 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.23 (1 H, m), 3.90 (1 H, m), 3.4–2.9 (2 H, m), 2.4–1.5 (10 H, complex); mass spectrum, *m/e* (relative intensity) 182 (5, M$^+$), 164 (7), 79 (100).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.82; H, 7.29.

4-*anti*-Hydroxy-1-isopropyl-2-oxaadamantane (6). A 300-mg sample of **1a**[1] (1.53 mmol) was added to 50 mL water. Then 25 mL of concentrated sulfuric acid was added dropwise, and the mixture was stirred overnight at room temperature. After dilution with another 50-mL portion of water, the mixture was extracted with methylene chloride. The organic layer was washed with sodium bicarbonate and water and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave an oily crude product. Chromatographic purification yielded 228 mg (76%) of **6** as a white solid: mp 71 °C; IR ($CHCl_3$) 3400 (OH), 2930, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (2 H, m), 2.70 (1 H, s), 2.3–1.2 (11 H, complex), 0.87 (6 H, d[19]); mass spectrum, *m/e* (relative intensity) 196 (17, M$^+$), 153 (10), 110 (100).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.49; H, 10.30.

1-Isopropyl-2-oxaadamantan-4-one (7). A 125-mg sample of **6** (0.64 mmol) was oxidized according to Jones' procedure,[7] giving 78 mg (63%) of **7** as a colorless liquid: IR ($CHCl_3$) 2940, 1720, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.91 (1 H, m), 2.65 (1 H, m), 2.5–1.3 (10 H, complex), 0.86 (6 H, d); mass spectrum, *m/e* (relative intensity) 194 (27, M$^+$), 166 (66), 123 (59), 122 (55), 79 (100).

4-*anti*-Chloro-1-isopropyl-2-oxaadamantane (8). A 98-mg sample of **1a** (0.50 mmol) was refluxed for 72 h in an excess of thionyl chloride which was not freshly distilled. After cooling, the mixture was poured onto ice-water and extracted with methylene chloride. The organic layer was washed with sodium bicarbonate and water, dried over anhydrous magnesium sulfate, and evaporated. Purification by column chromatography afforded 103 mg (96%) of **8** as a colorless liquid: IR ($CHCl_3$) 2950, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.5–3.9 (2 H, complex), 2.5–1.1 (11 H, complex), 0.86 (6 H, d); mass spectrum, *m/e* (relative intensity) 214/216 (17/5, M$^+$), 179 (11), 171 (12) 128 (100).

Anal. Calcd for $C_{12}H_{19}ClO$: C, 67.12; H, 8.92. Found: C, 67.43; H, 8.71.

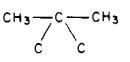
4-*anti*-Chloro-5,5-dimethyl-4-oxa-5-homoadamantane (9a). A 93.6-mg sample of **1a** (0.48 mmol) was refluxed in 7 mL of freshly distilled and purified thionyl chloride for 2 h. The reaction mixture was poured onto ice-water, and the usual workup with methylene chloride gave 77.6 mg (76%) of **9a** as a colorless liquid: IR ($CHCl_3$) 2850, 1440, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.3–4.2 (1 H, m), 2.5–1.35 (12 H, complex), 1.30 (3 H, s), 1.28 (3 H, s); mass spectrum, *m/e* (relative intensity) 199/197 (34/9), 179 (4), 121 (36), 79 (74), 59 (100).

Anal. Calcd for $C_{12}H_{19}ClO$: C, 67.12; H, 8.92. Found: C, 66.75; H, 8.65.

2-*anti*-Chloro-4-oxa-5-homoadamantane (9b). A 114-mg sample of **1b** (0.68 mmol) treated as described for the synthesis of **9a** gave 108 mg (86%) of **9b** as a colorless liquid which slowly

(18) T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **36**, 3460 (1971).

(19) The distance of the two signals (6.5 Hz) is not field dependent. This proves that the splitting is due to vicinal hydrogen–hydrogen coupling; the two signals do not represent two nonequivalent methyl groups in a moiety as shown below (as, e.g., in **1a**).



crystallized: mp 129 °C; IR ($CHCl_3$) 2970, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.10 (2 H, m), 3.85 (1 H, s), 2.6–0.6 (11 H, complex); mass spectrum, m/e (relative intensity) 188/186 (11/36), 79 (100).

4-*anti*-Bromo-1-isopropyl-2-oxaadamantane (10). A 350-mg sample of **1a** (1.77 mmol) was treated with thionyl bromide as described for the synthesis of **8**. The yield was 118 mg (26%) of **10** as a yellowish oil: IR ($CHCl_3$) 2950, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.55 (1 H, m), 4.04 (1 H, m), 2.6–1.1 (11 H, complex), 0.88 (6 H, d); mass spectrum, m/e (relative intensity) 260/258 (15/16, M^+), 217/215 (7/7), 179 (17), 174 (51), 172 (54), 123 (70), 91 (90), 43 (100).

2-*anti*-Iodo-4,4-dimethyladamantane (23). A 185-mg sample of **1a** (0.93 mmol) was refluxed overnight in 57% hydriodic acid. After cooling the reaction mixture was diluted with water and extracted with methylene chloride. After the usual workup, 149 mg (52%) of **23** as a colorless liquid was obtained which turned dark after some hours at room temperature: IR ($CHCl_3$) 2950, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (1 H, m), 2.5–1.2 (12 H, complex), 1.10 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 47.0 (C^3), 44.6 (C^2), 39.0 (C^4), 37.4 (C^1), 36.7 (C^5), 34.9 (C^8), 34.7 (C^9), 34.1 (C^6), 28.8 (C^{10}), 28.5 (C^7), 27.5 ($2CH_3$); mass spectrum, m/e (relative intensity) 163 (100) ($M^+ - I$).

2-*anti*-Bromo-4,4-dimethyladamantane. A 158-mg sample of **1a** (0.81 mmol) was refluxed overnight in 48% hydrobromic acid. After cooling, the reaction mixture was diluted with water and extracted with methylene chloride. The usual workup afforded 33 mg (16%) of 2-*anti*-bromo-4,4-dimethyladamantane as a colorless liquid: IR ($CHCl_3$) 2950, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.12 (1 H, m), 2.5–1.2 (12 H, complex), 1.10 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 61.7 (C^2), 45.7 (C^3), 38.9 (C^4), 36.4 (C^5), 36.1 (C^1), 34.6 (C^9), 33.6 (C^6), 33.2 (C^8), 28.1 (C^{10}), 27.4 ($2CH_3$), 27.1 (C^7); mass spectrum, m/e (relative intensity) 163 (100) ($M^+ - Br$).

Adamantane-2,4-dione (17). A 200-mg sample of **1c** (1.10 mmol) were dissolved in 20 mL water and 25 mL concentrated sulfuric acid. The mixture was refluxed overnight, and after it cooled, 50 mL water was added. The usual workup with chloroform afforded 50 mg (22%) of **17** as a white solid: mp 282–283 °C; IR ($CHCl_3$) 2940, 2860, 1730, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.40 (1 H, m), 2.76 (2 H, m), 2.5–1.5 (9 H, complex); ^{13}C NMR ($CDCl_3$) δ 207.6 ($C^{2/4}$), 68.3 (C^3), 45.0 ($C^{1/5}$), 44.0 (C^{10}), 38.2 ($C^{6/8}$), 30.0 (C^9), 26.0 (C^7); mass spectrum, m/e (relative intensity) 164 (100, M^+), 136 (14), 79 (78).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.08; H, 7.54.

The ^{13}C NMR data of 4-oxa-5-homoadamantane derivatives will be published in a forthcoming paper.

Acknowledgment. We are indebted to Professor Dr. E. Wenkert for helpful discussions. We are also grateful to Dr. D. Müller (Bochum) for recording the mass spectra as well as to Mrs. E. Sauerbier for her skillful assistance in some syntheses. This work was supported by the Fonds der Chemischen Industrie.

Registry No. **1a**, 66483-57-6; **1b**, 66483-52-1; **1c**, 79499-77-7; **6**, 78726-35-9; **7**, 78726-38-2; **8**, 78726-36-0; **9a**, 79499-78-8; **9b**, 79499-79-9; **10**, 78726-37-1; **12a**, 79499-80-2; **17**, 19214-00-7; **19a**, 79548-72-4; **19b**, 79499-81-3; **19c**, 56820-19-0; **21**, 18971-91-0; **23**, 79499-82-4; **24**, 56781-86-3; **25**, 56781-85-2; *endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid, 21932-98-9; 2-*anti*-bromo-4,4-dimethyladamantane, 79499-83-5.

Vinyl Cations. Comparison of Gas-Phase Thermodynamic and Solvolysis Data with ab Initio MO Calculations

Herbert Mayr,* Reinhard Schneider, Dieter Wilhelm, and P. v. R. Schleyer

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany

Received July 1, 1981

Ab initio MO calculations with the STO-3G basis set level on cyclic and acyclic methyl- and phenyl-substituted vinyl cations have been used, in combination with the experimental heat of formation of the parent vinyl cation, to evaluate $\Delta H_f°$ values for a set of vinyl cations. Comparison of these thermodynamic values with solvolysis data shows that only one-quarter of the stabilizing influence of substituents is effective in the solvolysis transition states. The slow solvolysis rates of vinyl compounds are thus not primarily due to the low stability of vinyl cations but to an unusually high kinetic barrier between vinyl derivatives and the corresponding ionic intermediates.

A knowledge of relative carbenium ion stabilities is essential for the interpretation of reactions involving carbocations and is being used to help design syntheses via cationic intermediates.[1] In principle, such relative stabilities may be obtained from solvolysis data or from thermochemical studies. However, only a few gas-phase heats of formation have been determined. Utilization of reactivity data in solution requires that solvolysis transition states resemble the corresponding carbenium ions energetically. Furthermore, published solvolysis rates have been measured under different conditions with varying leaving groups so that a consistent set of data is not available. Therefore, we have now used molecular orbital calculations to gather such thermochemical information.

Earlier computational treatments of vinyl cations concentrated on structures and the relative stabilizing abilities of α or β substituents.[2] We now extend this work on polysubstituted and cyclic systems in order to obtain heats of formation of vinyl cations with widely varying substitution patterns (**1–13**).

Calculations were carried out at the restricted Hartree–Fock level by using the ab initio SCF–MO GAUSSIAN 70 series of programs.[3] Partial geometry optimizations

(1) (a) Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 184. (b) Mayr, H.; Schütz, F. *Tetrahedron Lett.* **1981**, 925. (c) Mayr, H.; Seitz, B.; Halberstadt-Kausch, I. K. *J. Org. Chem.* **1981**, *46*, 1041.

(2) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004. (c) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901. (d) Apeloig, Y.; Collins, J. B.; Cremer, D.; Bally, T.; Haselbach, E.; Pople, J. A.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 3496. (e) Krishnan, R.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(3) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A.; QCPE Program No. 236, Indiana University Bloomington, IN.

0022-3263/81/1946-5336$01.25/0