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AB INITIO MO CALCULATIONS ON THE REARRANGEMENTS OF 7-OXA-2-BICYCLO[2.2.1]HEPTYL CATIONS. THE FACILE MIGRATION OF ACYL GROUP IN WAGNER–MEERWEIN REARRANGEMENTS

PIERRE-ALAIN CARRUPT AND PIERRE VOGEL*

Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005 Lausanne (Switzerland)

ABSTRACT

Ab initio STO-3G and 6-31G minimized geometries of 5-oxo- (**9**), 6-oxo-7-oxabicyclo[2.2.1]hept-2-yl cation (**12**) and 7-oxabicyclo[2.2.1]hept-2-yl cation (**15**) were obtained. The energy barriers for their Wagner–Meerwein rearrangements to the more stable 5-oxo- (**11**), 6-oxo-3-oxabicyclo[2.2.1]hept-2-yl (**13**) and 3-oxabicyclo[2.2.1]hept-2-yl (**17**) cations, respectively, have been evaluated and compared with those calculated for the rearrangement of the 5-oxo (**18**) and 6-oxobicyclo[2.2.1]hept-2-yl cations (**20**). In agreement with experimental data, the 'true migratory aptitude' of an acyl group is higher than that of β-oxoalkyl group in competitive Wagner–Meerwein rearrangements that are 'energetically unbiased'. The ease of the acyl group 1,2-shift toward an electron-deficient center is related to the electron-donating ability of the carbonyl group due to favorable $n(CO) \leftrightarrow \sigma \leftrightarrow p(C^+)$ hyperconjugative interaction.

INTRODUCTION

1,2-Shifts of electron-withdrawing groups such as RCO[1,2] or COOR[3,4] groups toward electron-deficient centers have been observed in several carbenium ion rearrangements. This was possible because alternative migrations of hydride, alkyl or aryl groups would have led to much less stable carbenium ion intermediates. In the presence of HSO_3F/Ac_2O in CH_2Cl_2, 2-exo-cyano- (**1a**) and 2-endo-cyano-5,6-exo-epoxy-7-oxabicyclo[2.2.1]hept-2-yl acetate (**1b**) gave products derived from the 3-oxabicyclo[2.2.1]hept-2-yl cation intermediates **2**. The latter arise from the epoxide ring opening and 1,2-shift of the β-substituted alkyl group (bond σC(3,4)). No products deriving from the isomeric intermediates **3** could be observed. In contrast, and under similar conditions, the 5,6-exo-epoxy-7-oxabicyclo[2.2.1]hept-2-one (**4**) gave the diacetates **6** derived from the intermediate **5**. In this case, the 1,2-shift of the acyl group (**4** → **5**) was at least 30 times as fast as the 1,2-shift of the alkyl group (**4**→**7**) giving product **8**.[5] The following order of migratory aptitudes for 1,2-shifts toward electron-deficient centers was thus established: acyl > alkyl > alkyl α-substituted with inductive groups.

*Author for correspondence

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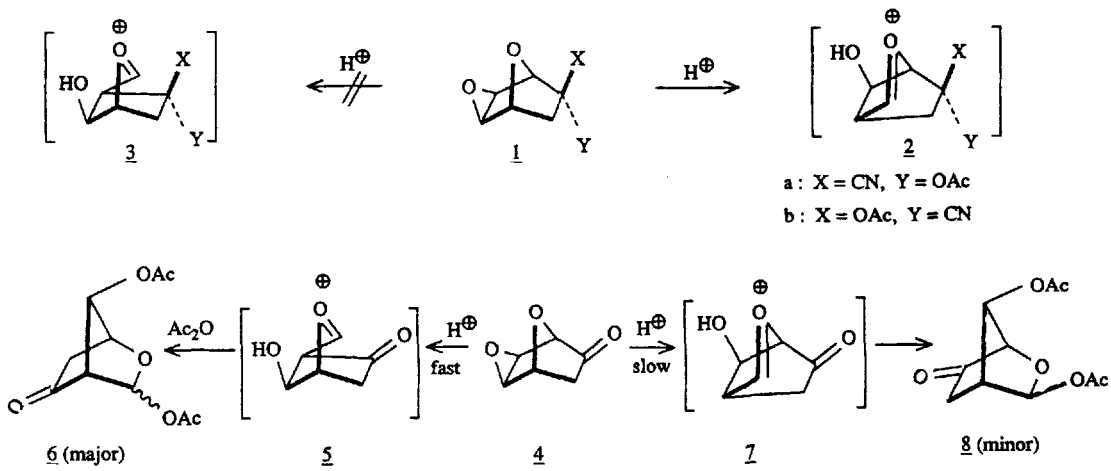
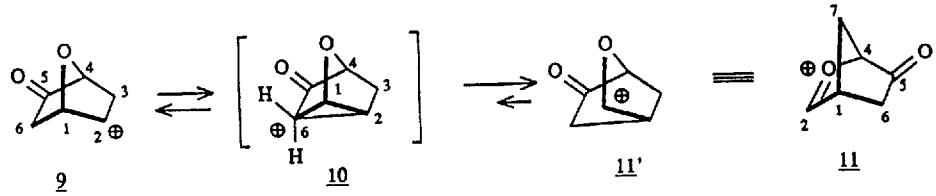


Because the isomeric pairs of ions **2** and **3**, on one hand, and, **5** and **7**, on the other hand, were expected to have similar stabilities (hypothesis 1), and since the rearrangements **1** → **2**, **1** → **3**, **4** → **5**, and **4** → **7** must all be exothermic reactions (hypothesis 2), we proposed[5] that the above data establish the 'true' migratory aptitudes of the acyl, alkyl, and α-substituted alkyl groups in an 'energetically unbiased' situation.[6]

We shall show in this work that *ab initio* MO calculations on model cations confirm the above hypotheses. Furthermore, our calculations indicate that the high migratory aptitude of an acyl group in a Wagner–Meerwein rearrangement is related to a hyperconjugative mechanism of the type n(CO) ↔ σ ↔ p(C^+) which is proposed to be responsible for the electron-donating ability of the carbonyl group homoconjugated with an electron-deficient π system.[7]

CALCULATION METHODS

Ab initio MO calculations with the STO-3G and 6-31G basis sets[8] were carried out using the MONSTERGAUSS 81 program[9a] on a CYBER 170-855 CDC computer, or the GAUSSIAN 82 program[9b] on a CRAY 1S or a NAS XL60 computer. The geometries were fully optimized with respect to all bond lengths and bond angles using Davidon's method[10] with standard convergence criteria at the STO-3G and 6-31G levels. In the case of saddle point structures (transition states) the VA05 method[11] was applied. Energies for geometries optimized by the 6-31G basis set were also calculated (single point) with the 6-31G* basis set (6-31G*//6-31G calculations). It is found that restricted basis sets predict a C_1 (classical, with little σ-bridging) structure for bicyclo[2.2.1]hept-2-yl (norborn-2-yl) cation, whereas extended basis sets including polarization functions together with configuration interactions predict a C_s (non-classical, σ-bridged) structure for this cation.[12,13] Because of the oxygen atom in 7-oxa- and 3-oxanorborn-2-yl cations we were not so much concerned about a 'true' estimation of the amount of σ-bridging in these species. For that reason, and also because of the size of the molecules investigated, we indulged ourselves in using restricted basis sets without including electron correlation effects.



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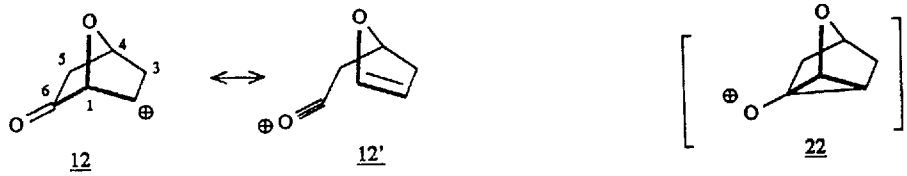

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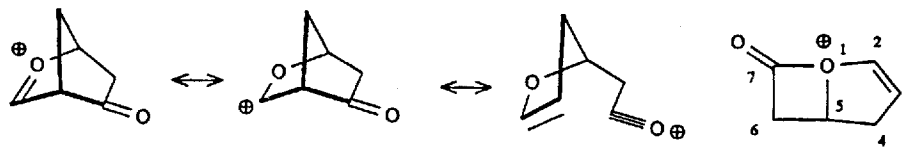

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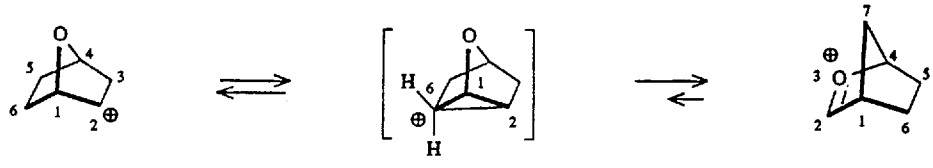

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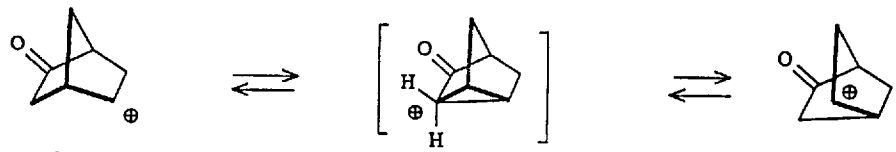

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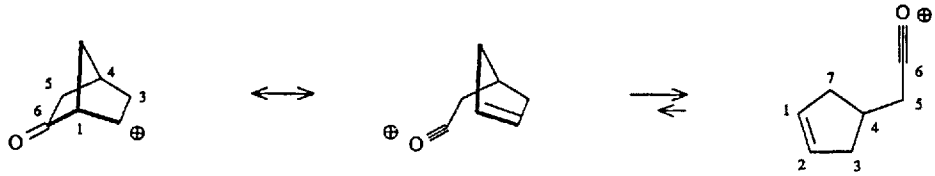


20 20' 21

Table 1. Total energies (hartrees) and relative energies (kcal/mol) of cations **9–21**

Basis set	STO-3G[a]		6–31G[a]		6–31G*b	
9	−375·93109	43·2	−380·48227	30·8	−380·66244	35·2
10	−375·92145	49·6[c]	−380·47530	35·5[c]	−380·66129	35·9
11	−375·99158	3·0	−380·52466	4·2	−380·71211	4·0
12	−375·94304	35·7[c]	−380·48522	29·0	−380·66893	31·1
13	−376·00000	(0·0)	−380·53140	(0·0)	−380·71849	(0·0)
14	−375·98984	6·7	———	———	———	———
15	−303·29747	40·8	−306·85612	28·5	−306·99441	31·8
16	−303·29289	43·6[c]	−306·85577	28·8[c]	−306·99586	30·9
17	−303·36241	(0·0)	−306·90161	(0·0)	−307·04516	(0·0)
18	−340·68965	7·0	−344·71865	9·2	−344·87264	15·6
19	−340·67814	14·1[c]	−344·71172	13·5[c]	−344·87014	17·2
20	−340·70079	(0·0)	−344·72137	7·5	−344·87951	11·3
21	−340·69080	6·3	−344·73324	(0·0)	−344·89748	(0·0)

[a]With complete geometry optimization
[b]Single point (6-31G geometry) calculations
[c]Transition state, one negative eigenvalue

RESULTS AND DISCUSSION

The calculated total energies of cations **9–21** are reported in Table 1.

As expected the Wagner–Meerwein rearrangements of the 7-oxanorbon-2-yl cations **9**, **12** and **15** into the corresponding 3-oxanorborn-2-yl cations **11**, **13** and **17**[14] are highly exothermic processes (cf. gas phase heterolytic bond dissociation enthalpies $DH°(CH_3CH_2CH_2^+/H^-)$ = 267 kcal/mol, $DH°(CH_3OCH_2^+/H^-)$ = 243 kcal/mol[15]). The calculated exothermicity of equilibrium **9** $\rightleftarrows$ **11** (31·0 kcal/mol (6-31G*)) does not differ significantly from that obtained for **12** $\rightleftarrows$ **13** (31·1 kcal/mol (6-31G*)). Moreover, they are about the same as that calculated for the unsubstituted derivatives **15** $\rightleftarrows$ **17** (30·9 kcal/mol (6-31G*)). These data confirm our hypotheses, 1 and 2, for the interpretation of the stereoselectivity of the acid-promoted rearrangement of 2,3-exo-epoxy-7-oxanorbornan-2-one (**4**). The order observed for the 1,2-shifts of acyl group (**4** → **5**) > β-ketoalkyl group (**4** → **7**) corresponds, indeed, to the 'true' migratory aptitude of these groups.

Energy barriers for the Wagner–Meerwein rearrangements

The rearrangement **9** $\rightleftarrows$ **11** involves the bridged cation **10** which was calculated to be a transition state (Table 1). The existence of an energy barrier for the reaction **9** $\rightleftarrows$ **11** is probably due to the inductive effect of the 5-oxo group in **9**. This hypothesis was supported by our calculations on the rearrangement of the non-substituted 7-oxanorborn-2-yl cation (**15**) into the 3-oxanorborn-2-yl cation (**17**) and also by the solvolyses of 2-chloro-7-oxanorbornanes reported by Martin and Bartlett.[14a] These reactions are slower than those of the corresponding 2-chlorononorbornanes due to the inductive effect of the oxygen atom. With the STO-3G and 6-31G basis sets, the 'classical' species **15** was found to be 2·8 and 0·7 kcal/mol, respectively,

more stable than the bridged ion **16**. This is somewhat lower than the energy differences calculated for **9** $\rightleftarrows$ **10** ΔE = 6·1 (STO-3G), and 4·4 kcal/mol (6-31G, see Table 1). Under solvolytic conditions, it is known for norborn-2-yl derivatives that substitution at C(5) and/or C(6) with electron-withdrawing groups leads to a diminution of the C(1)–C(6) participation in the bridged intermediates[16a] and even to an increased energy barrier for the Wagner–Meewein rearrangement.[16b]

In contrast, the acyl group migration **12** → **13** seems to occur without activation energy. We were not able to locate any transition state such as **22** for this rearrangement! With the 6-31G basis set, **12** corresponds to a shallow energy minimum. With the minimal STO-3G basis set, **12** was a saddle point. When the bond length C(1)—C(6) in **12** was chosen $\leqslant$ 1·8 Å, this cation 'relaxed' into the energy minimum **13**. However, when this starting distance was $\geqslant$ 2·5Å, the calculations yielded another energy minimum corresponding to the oxonium ion **14**, which was slightly less stable than **13**.

We have also examined the rearrangements of the 5-oxo (**18**) and 6-oxonorborn-2-yl cation (**20**). The symmetrically bridged cation **19** was calculated to be the transition state of the degenerate Wagner–Meerwein rearrangement **18** $\rightleftarrows$ **18′**. No such species could be located for the fragmentation **20** $\rightleftarrows$ **21** applying the various transition state localization algorithms supplied with MONSTERGAUSS and GAUSSIAN 82 programs. 'Manual localization' of a transition state starting with geometries of **19** or **20** failed also and led exclusively to the more stable pentenylethanoyl cation **21**. The calculations indicate that the 'true' migratory aptitude of an acyl group is better than that of the β-oxoalkyl group.

The electron-donating effect of homoconjugated carbonyl groups

Comparison of the calculated energies of **9** and **12** indicated the 6-oxo-7-oxanorborn-2-yl cation to be more stable than its 5-oxo isomer. If one considers the inductive (field) effect of the carbonyl group in these molecules, our results might be surprising because the distance between the positively charged center and the carbonyl dipole is shorter in **12** than in **9**. The comparison of the calculated geometries of these ions indicate, however, that there is a significant hyperconjugative (stabilizing) interaction n(CO) ↔ σC(1), C(6) ↔ p^+C(2) which compensates for the field (destabilizing) effect of the carbonyl group in **12**. This interaction can be represented by the canonical formula **12** ↔ **12′**. Indeed, the C(1)—C(2) bond in **12** is calculated to be significantly shorter (1.424 Å, 6-31G) than that in **9** (1·473 Å). Furthermore, the C(1)—C(6) bond in **12** is calculated to be extra-long (1·696 Å) and slightly elongated (1·589 Å) in **9** (Table 2). The same features are revealed on comparing the energies and geometries of the norborn-2-yl cations **18** and **20** (Tables 1–3).[7a] Interestingly, although the 3-oxanorborn-2-yl cations **11** and **13** are 'delocalized' oxy-substituted carbenium ions[17] (see e.g. **13** ↔ **13′**), the calculations predicted **13** to be more stable than **11**. Furthermore, the C(1)—C(6) bond (1·577 Å, 6-31G, Table 2) in **13** is calculated to be longer than the corresponding C(4)—C(5) bond (1·517 Å) in **11**, the C(1)—C(2) bond in **13** (1·488 Å) is found to be shorter than that in **11** (1·493 Å). These data also indicate that the carbonyl group in **13** stabilizes this species because of a hyperconjugative interaction of type **13′** ↔ **13″**. Homoconjugative interaction of the CO group as pictured with **22** must not be sufficiently large to render this function net electron-donating. This conclusion was confirmed by our calculations which indicated 'normal' C(2)—C(6) interatomic distances in **12**, **13**, and **20** (Tables 2 and 3).

Table 2. Interatomic distances in Å (6-31G)[a]

	(C1—C2)	(C1—C6)	(C2—C6)	(C1—O7)	(C=O)	(C4—C5)
9	1·473	1·589	2·375	1·441	1·200	1·523
10	1·392	1·842	2·090	1·384	1·199	1·517
11	1·493	1·578	2·410	1·263	1·198	1·532
12	1·424	1·696	2·315	1·423	1·181	1·533
13	1·488	1·577	2·393	1·261	1·195	1·525
15	1·440	1·650	2·262	1·422	—	1·535
16	1·407	1·756	2·164	1·400	—	1·535
17	1·487	1·587	2·402	1·260	—	1·530
18	1·449	1·622	2·328	1·560	1·203	1·528
19	1·387	1·929	1·929	1·520	1·201	1·504
20	1·408	1·759	2·326	1·554	1·177	1·538
21	1·331	2·988	3·010	1·527	1·114	1·546

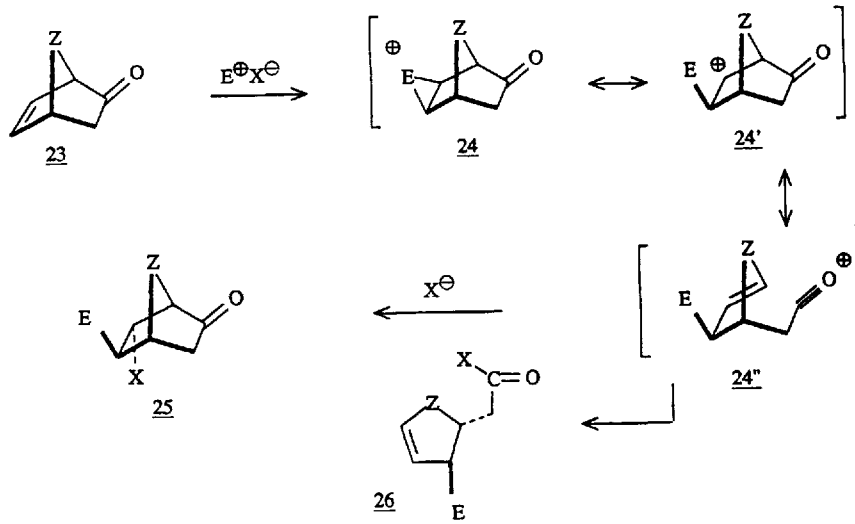
[a]Complete specifications of all geometries are available as supplementary material from the author.

Table 3. Interatomic distances in Å (STO 3G)[a]

	(C1—C2)	(C1—C6)	(C2—C6)	(C1—C7)	(C=O)	(C4—C5)
9	1·516	1·585	2·398	1·446	1·209	1·563
10	1·418	1·755	1·966	1·409	1·208	1·557
11	1·531	2·434	1·567	1·279	1·209	1·573
12	1·427	1·753	2·263	1·429	1·192	1·552
13	1·517	2·411	1·594	1·282	1·206	1·551
15	1·500	1·603	2·338	1·440	—	1·554
16	1·421	1·749	1·994	1·410	—	1·553
17	1·525	2·425	1·574	1·279	—	1·555
18	1·486	1·593	2·338	1·558	1·210	1·553
19	1·403	1·828	1·828	1·539	1·208	1·544
20	1·426	1·716	2·245	1·550	1·196	1·545
21	1·310	3·040	3·060	1·527	1·141	1·554
	(C6—C7)	(C1—C7)	(C4—C7)	(C=O)	(C1—C2)	
14	1·541	1·456	1·496	1·182	1·309	

[a]complete specifications of all geometries are available as supplementary material from the author.

Under these conditions of kinetic control, the electrophilic additions to bicyclo[2.2.1]hept-5-en-2-one, bicyclo[2.2.2]oct-5-en-2-one[7b] and 7-oxabicyclo[2.2.1]hept-5-en-2-one[7c] yielded adducts **25** exclusively, or under highly ionizing and low nucleophilic media, the products of C(1)—C(2) bond leakage **26**. The results were interpreted in terms of the intermediate **24** in which the carbonyl group plays the role of an electron-donating substituent as pictured with the canonical structures **24′** ↔ **24″**.[7a] This hypothesis has now been examined by *ab initio* calculations on a simpler model system: the 3-oxo-1-propyl cation. In a preliminary study,



Dixon *et al.*[18] calculated an extra-long C(2)—C(3) bond in 3-oxo-1-propyl cation with conformation **27** in which the 2*p* orbital at C(1) is in the plane of centers C(1), C(2), C(3), O. The calculations thus were in agreement with the intervention of a hyperconjugative interaction represented by the canonical formula **27** ↔ **27'**.

Employing more extended basis sets we have explored the energy hypersurface of species $C_3H_5O^+$ in somewhat more detail. The geometries **27–34** (see Figure 1, Table 4) were optimized completely at the closed-shell restricted Hartree–Fock (RHF)[19] level using first the minimal basis set STO-3G.[9] With the latter, the 6 different conformations **27**, **29–33** of the 3-oxo-1-propyl cation were all energy minimum. The geometries were then minimized with the basis sets 4-31G, 4-31G*, 6-31G and finally 6-31G*.[9b] Energy refinements were obtained by single-point calculations with the 6-31G** basis at the 6-31G* optimized geometries. The effects of electron correlation were estimated by the use of the second-order (MP2/6-31G**) and fourth-order (MP4/6-31G**) Møller–Plesset perturbation theory[20] at the 6-31G* optimized geometries of structures **27–30** for which pertinent geometry parameters are shown in Figure 1. Complete specifications of all geometries are available as supplementary material from the author. Conformers **31–33** of the 3-oxo-1-propyl cation were not energy minimum with the larger basis sets. As expected, one of the most stable isomers was found to be the planar oxet-2-yl cation **28** This cation is the global minimum of the hypersurface at the STO-3G level (ΔE(**28–35**) = −12·9 kcal/mol), but not with the higher levels used. At this level, the cation **35** is the global minimum (ΔE(**28–35**) = +16·4 kcal/mol with 6-31G* basis set).[21] The relative stability of the various conformers of 3-oxo-1-propyl cation (**27**, **29**, **30**) depended on the type of basis set used for the calculations. When neglecting electron correlation effects, the '*syn*-planar' conformer **29**, in which the 2*p* orbital of C(1) is

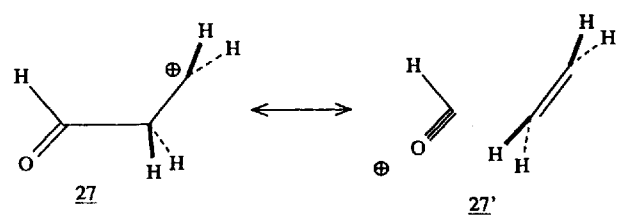


Table 4. Total energies (hartrees) and relative energies in parenthesis (kcal/mol) of $C_3H_5O^+$ (**27–34**)

	STO-3G	4-31G	4-31G*	6-31G	6-31G*	6-31G**[a]	MP2/6-31G**[a]	MP4/6-31G**[a]
27	−188·62103 (14·1)	−190·72153 (9·9)	−190·82577 (8·4)	−190·91802 (10·3)	−191·01089 (8·6)	−191·01969 (8·8)	−191·60440 (0·0)	−191·64077 (0·0)
28	−188·71862 (−47·1)	−190·75576 (−11·6)	−190·87564 (−22·9)	−190·95322 (−11·8)	−191·06118 (−22·9)	−191·06992 (−22·7)	−191·65608 (−32·5)	−191·69091 (−31·5)
29	−188·62503 (11.6)	−190·73733 (0·0)	−190·83919 (0·0)	−190·93445 (0·0)	−191·02464 (0·0)	−191·03375 (0·0)	−191·60242 (1·2)	−191·64013 (0·4)
30	−188·61809 (16·0)	−190·72622 (7·0)	−190·83109 (5·1)	−190·92343 (6·9)	−191·01566 (5·6)	−191·02494 (5·5)	−191·59992 (2·8)	−191·63719 (2·2)
31	−188·62775 (9·9)	[b]	[b]	[b]	[b]	[b]	[b]	[b]
32	−188·63030 (8·3)	[b]	[b]	[b]	[b]	[b]	[b]	[b]
33	−188·61887 (15·5)	[b]	[b]	[b]	[b]	[b]	[b]	[b]
34	−188·64360 (0·0)	−190·73251 (3·0)	−190·83478 (2·8)	−190·93024 (2·6)	−191·02029 (2·7)	−191·02931 (2·8)	−191·60267 (2·7)	−191·64047 (0·2)

[a]Single point energy calculations at the 6-31G* optimized geometries. (1 hartree = 627·5 kcal/mol).
[b]No related conformers were found as energy minima.

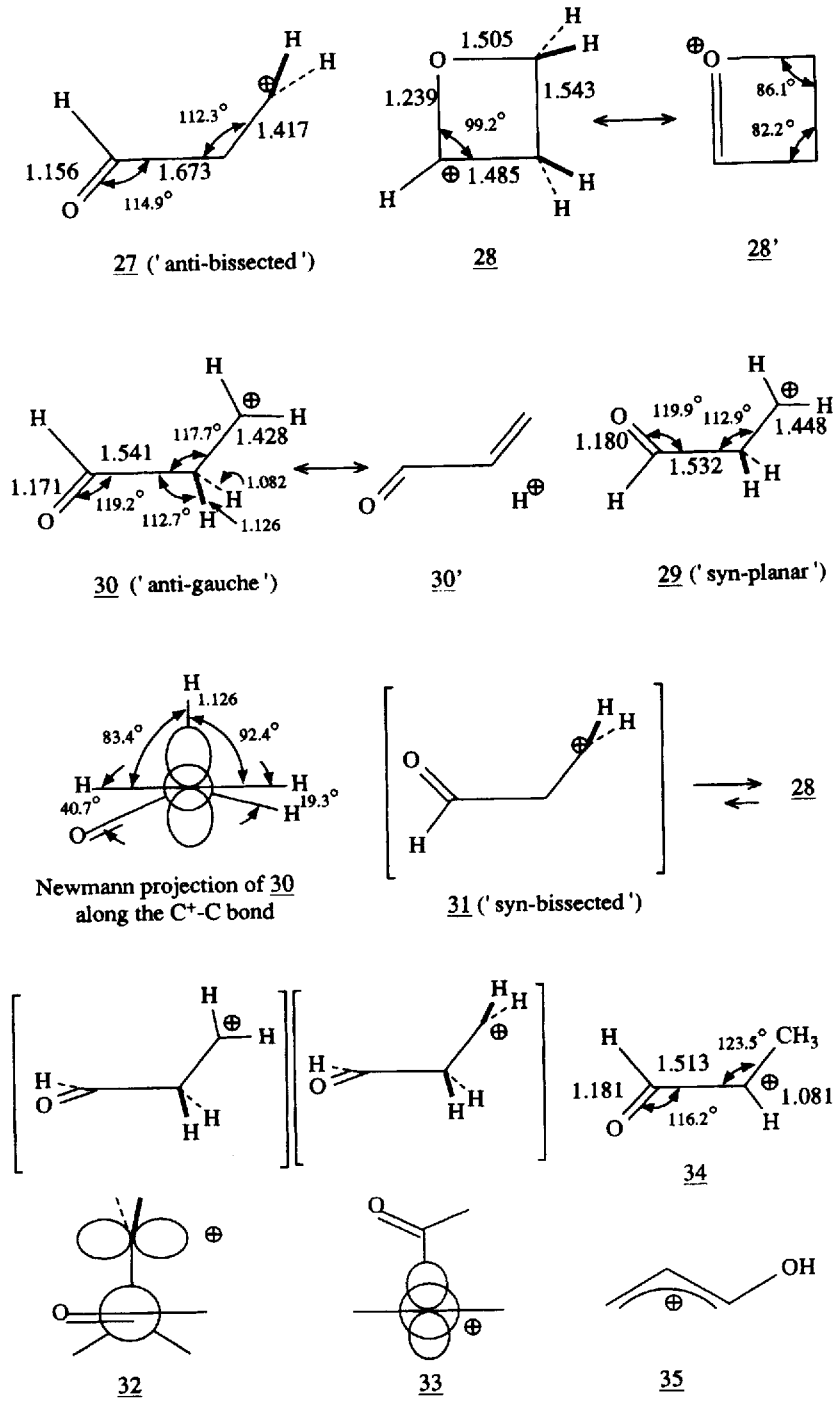


Figure 1. Geometries of $C_3H_5O^+$ optimized with the 6-31G* basis set. Structures **31–33** are minimum with the STO-3G basis set only. (Bond lengths in Å, bond angles in °)

perpendicular to the C(1), C(2), C(3), O plane and the oxygen atom *syn* with respect to C(1), was calculated to be the most stable one. When electron correlation effects were included (MP2 and MP4/6-31G** calculations) the '*anti*-bissected' conformer **27**, in which the 2*p* orbital and the oxygen atom *anti* with respect to C(1), was the most stable structure for 3-oxo-1-propyl cation. Rotamer '*syn*-bissected' **31** (the oxygen atom *syn* with respect to C(1)) was not an energy minimum at the higher levels employed. It cyclized into the more stable cation **28**.

Only the '*anti*-bissected' conformer **27** allows for a stabilizing n(O) $\leftrightarrow$ σC(2), C(3) $\leftrightarrow$ pC(1)$^+$ hyperconjugative interaction. Comparison of the 6-31G* optimized geometries of **27**, **29** and **30** confirmed that hypothesis. In the '*syn*-planar' conformer **29**, σC(2),C(3) $\leftrightarrow$ pC(1)$^+$ hyperconjugation is forbidden, thus the C(2)–C(3) bond is shorter in **29** than in **27**. The longer C=O bond in **27** than in **29** is also due to hyperconjugation **27** $\leftrightarrow$ **27'**. Interesting was the finding of the '*anti-gauche*' conformer **30** which allows for a 'reduced' n(O) $\leftrightarrow$ σC(2),C(3) $\leftrightarrow$ pC(1)$^+$ hyperconjugation compared with the '*anti*-bissected' structure **27**. This is manifested by the comparison of the bond lengths of C=O and C(2)—C(3) between **27**, **29** and **30**. The stability of **30** appeared to be due to a favorable hyperconjugative interaction between the pC(1)$^+$ orbital and one of the adjacent C—H bonds at C(2). The latter can be interpreted by limiting structures **30** $\leftrightarrow$ **30'** (Figure 1). It is not clear yet why a similar twist about C(1)—C(2) is not calculated for **29**.

Our calculations on $C_3H_5O^+$ cations are somewhat deceptive since they predict very little stability difference between the 3 conformers **27**, **29**, and **30** of 3-oxo-1-propyl cation. They demonstrate, however, the importance of electron correlation effects in discussing homoconjugative and hyperconjugative interactions between a carbenium ion and a carbonyl moiety. The relatively high stability of the '*syn*-planar' conformer **29** might be attributed to a favorable dipole (CO)/charge (C(1)$^+$) interaction which is not available in the '*anti*-bissected' conformer **27**. The 'acidifying' effect of the carbonyl function (**30** $\leftrightarrow$ **30'**) might be responsible for the favorable C—H/pC(1)$^+$ hyperconjugative interaction which stabilizes the '*anti-gauche*' conformer **30**.

CONCLUSION

In competitive Wagner–Meerwein rearrangements which are 'energetically unbiased', an acyl group migrates faster than a β-oxoalkyl group because the latter migration is retarded by the inductive effect of the carbonyl function. The ease of the acyl group 1,2-shift is related to the electron-donating ability of the carbonyl group when homoconjugated with an electron-deficient center. This stabilizing effect (related to the Grob fragmentation[22] and the frangomeric effect[23] can compete with the usual inductive (destabilizing) effect every time geometry of the molecule allows for an efficient n(CO) $\leftrightarrow$ σ $\leftrightarrow$ p hyperconjugative interaction[24] to intervene.

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