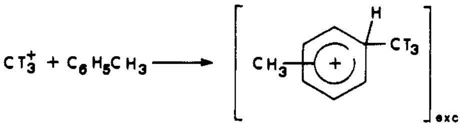
occur in a much shorter time than necessary for the formation of an organized solvation sphere, which requires, inter alia, rotational relaxation of dipolar molecules in the field of the cation.

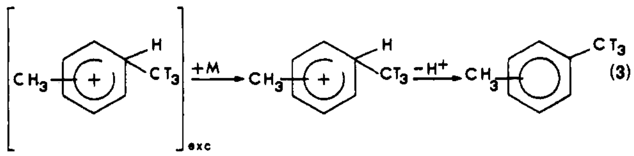
$$CT_4 \xrightarrow{\text{beta decay}} CT_3^+ + {}^3He + \beta^- \quad (1)$$

Several exothermic reaction channels are available to the decay methyl cation. Apart from hydride-ion abstraction, energetically allowed from both C_6H_6 and C_7H_8[7] and leading directly to the formation of partially tritiated methanes, alkylation of the arenes is also strongly exothermic, with a $\Delta H°$ value of the order of -100 kcal mol^{-1} for process 2.[8]



(2)

The highly excited arenium ions can either fragment, yielding for instance HT, partially tritiated methanes, etc., or be stabilized by the very effective collisional deactivation processes occurring in the liquid. The stabilized arenium ions can eventually lose a proton to any base contained in the system, including the substrate itself, thus giving the observed methylated products (eq 3), whose (relatively close) yields from C_6H_6 and C_7H_8 suggest that the rates of the alkylation and fragmentation processes are comparable for the two substrates.



(3)

Concerning the *substrate* selectivity of the reagent, the apparent[9] k_T/k_B ratio, referred exclusively to ring alkylation, i.e., to methyl for hydrogen substitution at the aromatic nucleus, can be approximately estimated from the results of the competition experiments. Interpretation of the data is complicated by the formation of appreciable amounts of tritiated toluene from C_7H_8, as well as from C_6H_6, which helps to explain the considerable scatter of the corrected k_T/k_B ratios obtained from a best fit treatment, i.e., 2.35, 2.19, and 2.39, respectively, for $[C_7H_8]$:$[C_6H_6]$ ratios of 10.0, 1.00, and 0.10.

The *positional* selectivity of the CT_3^+ attack is reflected by the isomeric composition of the xylenes, 40.1 ± 0.4% ortho, 27.0 ± 0.1% meta, and 32.9 ± 0.6% para from pure toluene, which underlines the electrophilic character of the alkylation and finds close analogies to the behavior of HeT^+, the only other free cation whose reactivity has been investigated in the liquid phase.[10]

To our knowledge, in the search to substantiate the long-postulated[11] role of carbonium ions in Friedel-Crafts alkylation, the present study provides the first data concerning a reagent whose +1 charge state and lack of a counterion are positively established *in the liquid phase.*[12] The approach outlined in the present communication appears of potential mechanistic value in order to evaluate the intrinsic reactivity of the most simple carbocation, unperturbed by the effects of the anion, the catalyst, etc., that have complicated all too frequently the study of aromatic alkylation.[13] Extension of the decay technique to the solid state is also conceivable. More detailed investigations on the electrophilic reactivity of *free* CT_3^+ decay ions, in particular a comparative study of their attack to gaseous and liquid arenes, are in progress and will be reported in due course.

Acknowledgments. We wish to thank Professor G. Stöcklin for his generous help and M. Schüller for his invaluable assistance in the radiochemical work. F.C. acknowledges the C.N.R. for the financial support.

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(5) The time required by a 5.6-keV β particle to reach a 100-Å distance from the decayed molecule is quite short, $<10^{-15}$ s. As no C–He bonding exists, see S. Wexler and D. C. Hess, *J. Phys. Chem.*, **62**, 1382 (1958), the primary decay fragment, $[^3HeCT_3]^+$, can be expected to dissociate into a free methyl ion in a time comparable with the period of a bond vibration, roughly 10^{-14} s.

(6) For instance, CH_3^+ condensates with CH_4 in the gas phase at a rate approaching collision frequency; see M. Henchman, "Ion-molecule Reactions," Vol. 1, J. L. Franklin Ed., Butterworths, London, 1972, p 177.

(7) The thermochemical calculations are based on gas-phase $\Delta H_f°$ values for CH_3^+ and the arenium ions, a rough approximation justified by the scarce degree of solvation of these species.

(8) Value arrived at by taking $\Delta H_f°$ 258 kcal mol^{-1} for CH_3^+ (see J. L. Franklin in "Carbonium Ions", Vol. 1, G. A. Olah and P. v. R. Schleyer Ed., Interscience, New York, N.Y., 1968, p 85) and assuming the PA of the methyl-substituted ring positions of the xylenes correspondent to that of toluene (see R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).

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(11) See for instance L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1940, and references therein.

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The Importance of Leaving Group Steric Effects in Solvolysis of Tertiary Carbinyl Systems Empirical Force Field Treatment of Acid-Catalyzed Dehydration of 2-Alkyl-2-adamantanols

Sir:

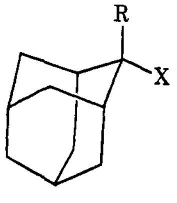
We wish to report that replacement of a methyl group by a *tert*-butyl group in 2-alkyl-2-adamantanols, **1**, increases the dehydration rate by a factor of 1820, whereas the *t*-Bu/Me ratio in the solvolysis of the corresponding *p*-nitrobenzoates, **2**, is 225 000.[1] Empirical force field calculations[2] show that the hydrocarbon-cation model is in good agreement with the dehydration data but leaving group steric effects are to a large extent responsible for the very high *t*-Bu/Me ratios in the solvolysis of strained tertiary carbinyl *p*-nitrobenzoates.

The steric requirements of OH and OPNB have frequently been stated to be similar, at least in norbornyl derivatives.[3] In the alkydi-*tert*-butylcarbinyl system, however, the *t*-Bu/Me ratio goes from 0.08 to 60 when the leaving group is changed from water[4] to OPNB.[5] The alkyldi-*tert*-butylcarbinols are highly congested species and, perhaps, atypical. We undertook therefore to reexamine the effect of replacing OH by OPNB in a more representative system.

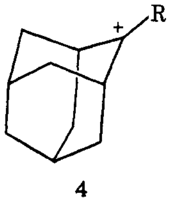
Table I. First-Order Rate Constants for Dehydration of 2-Alkyl-2-adamantanols, **1**, in Anhydrous Acetic Acid Containing 0.006 M Sulfuric Acid at 25 °C, Calculated Strain Energies for 2-Alkyladamantanes, **3**, and the Corresponding Cations, **4**

Compd	R	10^4k_1, s^{-1}	k_{rel}^{OH}	$k_{rel}^{OPNB\,a}$	Strain energies^b Hydrocarbon **3**	Strain energies^b Cation **4**
1-4a	Me	1.48	1.00	1.00	8.56	8.63
1-4b	Et	3.58	2.42	7.2	9.23	7.94
1-4c	*i*-Pr	1.57	1.06	33.5	10.91	8.57
1-4d	*i*-Bu	8.90	6.01		9.66	8.91
1-4e	*t*-Bu	2700^c	1820	225,000	16.25	12.24
1-4f	Neopentyl	18.2	12.3	10.0	11.42	9.81
1-4g	*t*-Am	4600^c	3200		18.95	13.92

^{a} Relative solvolysis rates of 2-alkyl-2-adamantyl *p*-nitrobenzoates, **2**, from ref 1. ^{b}Reference 8. ^{c} Reference 7.



1, X = OH
2, X = OPNB
3, X = H



4

Rate constants were determined for the sulfuric acid catalyzed dehydration of a series of 2-alkyl-2-adamantanols in anhydrous acetic acid at 25 °C (Table I).[6] The amplitude of the rate variation is less than in the solvolysis of the *p*-nitrobenzoates but, apart from the anomalously low reactivity of **1c** (R = *i*-Pr), the reactivity trend is much the same, as is shown by eq 1.

$$\log k_{rel}^{OPNB} = (1.62 \pm 0.22) \log k_{rel}^{OH} - 0.12 \quad \text{(correlation coefficient, } r = 0.983) \qquad (1)$$

Solvolytic reactivities of carbinyl halides, tosylates, triflates, and *p*-nitrobenzoates have been interpreted in terms of Δ strain, the difference in strain energy between the parent hydrocarbon and the corresponding carbonium ion, taken to represent the transition state.[1,9,10]

Alcohol dehydration rates,[11] expressed in terms of the differences in the free energies of activation, $\Delta\Delta G^{\ddagger}$ ($= RT \log_e k_{rel}^{OH}$) correlate fairly well with Δ strain, following eq 2:

$$\Delta\Delta G^{\ddagger} = (1.01 \pm 0.11)\ \Delta\,\text{strain} - 0.06 \quad \text{(correlation coefficient, } r = 0.977) \qquad (2)$$

The unit slope means that the effect of an alkyl substituent on the dehydration rate is completely accounted for by the associated strain energy change.[12] Either the hydrocarbon is a reasonable surrogate for the alcohol[14] and the dehydration transition state is close to the carbonium ion[15] or the errors in both approximations cancel out.

The solvolytic reactivities of the *p*-nitrobenzoates,[1] on the other hand, increase much faster than can be explained by Δ strain, the slope of the $\Delta\Delta G^{\ddagger}$ *vs.* Δ strain correlation being a rather implausible 1.77 ± 0.38. This is a clear indication that the OPNB group cannot be treated as a hydrogen atom and that front-strain[16] relief is of considerable magnitude in this system where the leaving group is axial to one of the cyclohexyl rings.

Brown et al. associate the high *t*-Bu/Me ratio observed in the solvolysis of 2-alkyl-2-adamantyl *p*-nitrobenzoates and also of 2-substituted *endo*-norbornyl (39 600) and *endo*-camphenilyl (1 120 000) *p*-nitrobenzoates with the "rigidity" of the parent system.[17] Our results, however, show that this ratio owes a great deal to leaving group steric effects, at least in the adamantyl system and probably in the others as well. Moreover, the following example shows that the simple concept of rigidity is misleading in highly crowded structures. In the alkyldi-*tert*-butyl-carbinyl system the *t*-Bu/Me ratio for solvolysis[5] is 60 which, according to the criterion of Peters and Brown,[17] places it between the flexible acyclic (4.4) and the slightly less flexible alicyclic systems (112 to 273). Nevertheless, it is hard to conceive of this as a flexible system when the parent hydrocarbons, 1,1-di-*tert*-butylethane and tri-*tert*-butylmethane, have estimated strain energies of 12-15 and 35-40 kcal/mol, respectively.[18] Both are more strained than the corresponding adamantane derivatives and, therefore, presumably more rigid.

The solvolytic reactivity of tertiary carbinyl systems is no doubt better understood in terms of strain energy changes but the empirical force field method has only recently been extended to carboxylic acids[19] and further refinements will be necessary before bulky carboxylate leaving groups can be handled explicitly.[20]

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(6) First-order rate constants (±1–4%) were measured conventionally.[4] Except for **1a,** the major reaction product was the corresponding olefin. Alcohols **1a** and **1b** gave also acetates. The 2-methyl-2-adamantyl cation, **4**a, reacts very readily with the solvent and even with product water, but at the alcohol concentration used (0.01 M) the kinetic plot was linear for at least two half-lives.
(7) Extrapolated from data at lower acidity.
(8) Data for **3a–c** and **3e** are taken from E. M. Engler, Ph.D. Thesis, Princeton University, 1973. Other hydrocarbons and all cations were calculated with the appropriate force field.[2b,9a] The data given as "strain energies" in ref 1 are "steric energies" according to the more recent definition[2b] and, as such, are underestimated.
(9) (a) G. J. Gleicher and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **89,** 582 (1967); (b) R. C. Bingham and P. v. R. Schleyer, *ibid.*, **93,** 3189 (1971); (c) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *ibid.*, **96,** 1969 (1974).
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(11) The deviation of alcohol 1**c,** not included in eq 2, is all the more surprising in that its *p*-nitrobenzoate solvolysis rate is in agreement with the strain energy calculations.[3] This point will be discussed elsewhere.
(12) As to the polar substituent effect, the inclusion of a polar contribution, $\rho^*\sigma^*$ where ρ^* is -3.3,[5,13] does not disimprove the strain energy correlation but reduces the slope to 0.79. For recent contributions to the σ^* controversy, see M. Charton, *J. Am. Chem. Soc.*, **97,** 3691 (1975); A. J. MacPhee and J. E. Dubois, *Tetrahedron Lett.*, 2471 (1976).
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Tetrahedron Lett., **407** (1976); for *o*-tolyldi-*tert*-butylcarbinols, −4.2 (J. S. Lomas, P. K. Luong, and J. E. Dubois, unpublished results).

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(20) A referee has requested comment upon the effect of the change of solvent from acetic acid (dehydration) to aqueous acetone (solvolysis) upon the rate comparisons. Transferring the solvolysis reaction to acetic acid would only affect the relative rates to the extent that Grunwald–Winstein *m* values or solvent nucleophilicity effects vary within the series. No such variation is to be anticipated: tertiary carbinyl derivatives solvolyze uniformly via an S_N1 mechanism and adamantyl systems are particularly immune to nucleophilic solvent participation. Relative solvolysis rates of alkyldi-*tert*-butylcarbinyl *p*-nitrobenzoates are slightly enhanced by solvent change from aqueous dioxane to acetic acid.[5]

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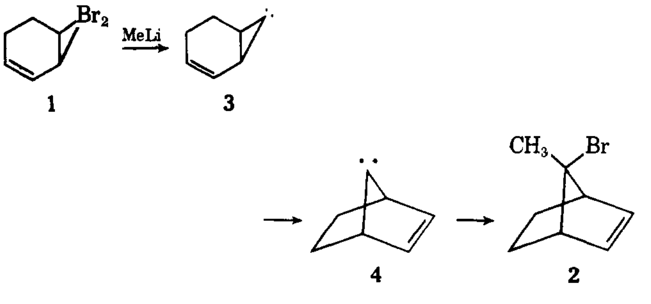
A Novel Carbene–Carbene Rearrangement

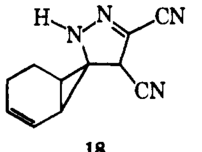
Sir:

The reaction of 7,7-dibromo-2-norcarene (**1**) with methyllithium gave as the main product *syn*-7-bromo-7-methylnorbornene (**2**).[1,2] It was proposed that formation of compound **2** involved rearrangement of 7-norcar-2-enylidene (**3**) to 7-norbornenylidene (**4**)[3] (Scheme I). Several cases of carbene-carbene rearrangements have been reported,[4] particularly in aromatic systems, but the interconversion of carbenes **3** and **4** would be a novel example. It was therefore of interest to attempt the generation of carbene **3** unambiguously and record its behavior. One way to accomplish this would be to treat the appropriate *N*-nitrosourea with base,[5] a reaction that has successfully generated cyclopropylidenes.[6] A diazotate is an intermediate in this reaction and it can be isolated as a salt under special conditions.[5]

From *anti*-7-carboxy-2-norcarene (**5**)[7] the corresponding urea **6**[8] was prepared in the usual way via the isocyanate in 65% overall yield. Oxidation of **6** at −78 °C with N_2O_4 in THF afforded a 79% yield of the *N*-nitrosourea **7**.[9] Treatment of **7** with $KOC(CH_3)_3$ in THF at −40 °C gave diazotate **8** as a light brown powder.[10] The salt reacted with excess methanol with evolution of nitrogen, giving *anti*-7-methoxynorbornene (**9**) and *endo*-2-methoxytricyclo[4.1.0.0^{3,7}]heptane (**10**) in a ratio of 2:1, identified by comparison with authentic samples.[11] The same products in a ratio of 3:1 were formed in a reaction of **8** with 2 equiv of methanol in pentane. On the other hand, decomposition of the salt **8** with excess acetic acid afforded *anti*-7-acetoxy-2-norcarene (**11**)[12] as the sole volatile product (Scheme II).

Scheme I





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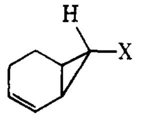
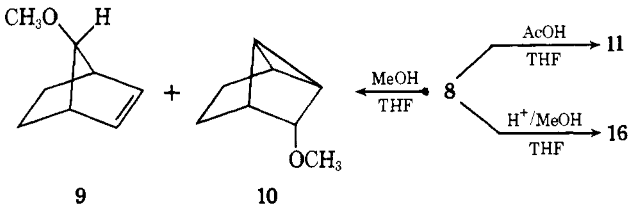


5, X = CO_2H
6, X = $NHCONH_2$
7, X = $N(NO)CONH_2$
8, X = N═NOK
11, X = $OCOCH_3$
13, X = $NH_2 \cdot HCl$
14, X = OCH_2CH_3
16, X = OCH_3

Scheme II



Different intermediates are apparently involved in these reactions. The formation of compound **11** is reasonably explained by internal return of an ion pair,[13] and the ethers **9** and **10** are those expected from the 7-norbornenyl cation (**12**) and methanol.[14] However, on the basis of our experiments it seems unreasonable that **12** results from a carbonium ion rearrangement.[15] Deamination of *anti*-7-amino-2-norcarene hydrochloride (**13**)[16] with sodium nitrite in THF/acetic acid afforded the acetate **11** (72% yield), besides several minor unidentified compounds. Furthermore, treatment of the diazotate **8** with $Et_3O^+BF_4^-$ [17] in ether/methylene chloride produced a complex mixture with the ether **14**[18] as the main component; <4% of the rearranged ether, *anti*-7-ethoxy norbornene (**15**), was found. A similar reaction of the diazotate **8** with 10 molar equiv of H_2SO_4 in excess methanol/THF afforded *anti*-7-methoxy-2-norcarene (**16**)[19] as the major product (75%) and no norbornene derivatives. When the latter reaction was carried out using D_2SO_4 in methanol-d_1/THF, no deuterium was incorporated into the product **16.** On the other hand, the decomposition of **8** in excess methanol-d_1 resulted in better than 97% incorporation of deuterium at C-7 of the ether **9**, as shown by the absence of a broad singlet at δ 3.12 (CCl_4). The ethers **9, 14, 15,** and **16** were unaffected by the reaction conditions.

Apparently, protonation of **8** results in formation of the corresponding diazonium ion which under acid conditions does not equilibrate with the diazo compound. Hence, products derived from the 7-norcar-2-enyl cation (**17**) are observed. On the other hand, basic conditions result in the diazo compound and, subsequently, the carbene **3** which rearranges to 7-norbornenylidene (**4**).[20] The latter should be nucleophilic rather than electrophilic, owing to interaction of the double bond with the electron-deficient carbon,[21] a conclusion that has recently been borne out by experiment.[22] Hence, protonation of **4** by methanol affords the carbonium ion **12**, from which the observed products **9** and **10** can be derived.

As expected the reaction of the *N*-nitrosourea **7** with $LiOCH_3$ in pentane[6] produced mainly a liquid (75%) which consisted of the ethers **9** and **10** in a ratio of 4:1 besides a small amount of *anti*-7-hydroxynorbornene.[23] The same products were isolated when pentane was replaced by *cis*-2-butene;[24] no addition to the double bond of the alkene was observed. Neither did the presence of diethyl fumarate result in formation of spiro compounds. Furthermore, we were not able to observe the expected color changes owing to formation of an intermediate diazo compound during any of the decomposition reactions; however, the base-induced decomposition of **7** in the presence of fumaronitrile gave the pyrazoline **18**[25] which is clear evidence for the presence of such an intermediate.

Our results contrast with those reported[26] for the decom-