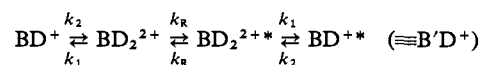


Figure 2. 100-MHz nmr spectrum of the ring protons of N,N'-di-*t*-butylpiperazinium dichloride at pD \leq 3.



In this case, the parameter $\alpha \approx 1 + (k'_N/k_2)[1 + (k_1/2k_R)]$ may have an unobserved dependence on pD, through k_1 ($k_1 = 10^4$ – 10^6 sec^{-1}), and because the unknown ratios k'_N/k_2 and k_1/k_R are not necessarily small. The possibility that I_R could be the rate-determining step must be rejected here, because $\tau = k'_N/(k_N k_R)$ would become independent of the pD. In the unlikely event of a primary I_N nitrogen inversion (with BD^+ and BD_2^{2+} in equatorial-axial chair conformations), the same equation is obtained and the same remarks can be made.

We may then infer that our results are evidence—however not yet sufficiently conclusive to exclude the other alternatives—for a double consecutive I_{NR} -type nitrogen inversion of the monocation with deuterium transfer, whose rate constant has the value $k_N = 2k_A = 3.10 \times 10^3 \text{ sec}^{-1}$. This is 100 times smaller than that obtained for P ($2 \times 10^5 \text{ sec}^{-1}$ at 44°C) for a supposed I_N inversion (and the parameter α equal to 1).

Acknowledgment. We thank Professor D. Gagnaire and his staff for the 100-MHz spectra on a Varian HA-100 apparatus and their helpful advice in analyzing them, and the referees for their pertinent remarks and their contribution in improving the quality of this text.

(8) J. L. Sudmeier and G. Occupati, *J. Am. Chem. Soc.*, **90**, 154 (1968).

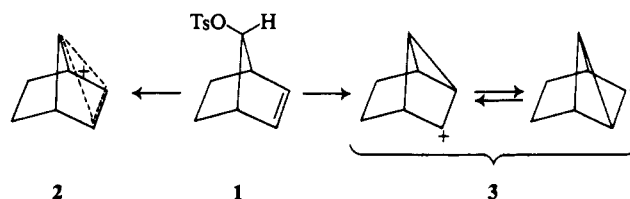
(9) To whom requests for reprints should be sent.

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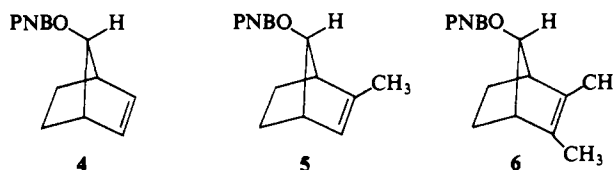
Evidence for the Symmetrical Nature of the 7-Norbornenyl Cation

Sir:

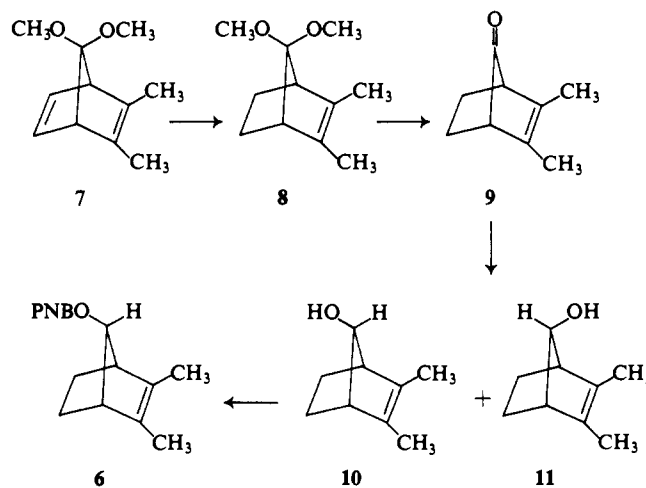
The cation derived from the solvolysis of *anti*-7-norbornenyl tosylate (**1**) has been described as both a symmetrical, highly delocalized species^{1,2} (**2**) and as a rapidly equilibrating pair of classical ions³ (**3**). We now report data which support the view that the acetolysis of **1** produces the ion **2** and not the rapidly equilibrating



pair of ions represented by **3**. Our position is based on a study of the rates and products obtained from the solvolysis of the series of *p*-nitrobenzoates, **4**, **5**, and **6**. We have found that the increase in rate in going from no methyl groups, to one methyl group, to two methyl groups on the double bond represents a "cumulative effect" of the methyls and not a "statistical effect" (which might be expected for the second methyl group if classical equilibrating ions were formed).



The *p*-nitrobenzoate **6** was prepared as shown below⁴



(1) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(2) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

(3) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

(4) Satisfactory elemental analyses have been obtained on all new compounds.

Table I. Solvolysis Rates of *anti*-7-Hydroxynorbornene *p*-Nitrobenzoates in 70:30 Dioxane-Water

Compound	Ref	Temp, °C	Rate, sec ⁻¹	k_n/k_4 140°	k_n/k_5 140°	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
4	7	185	1.38×10^{-4}	1	0.075	27.4	-17.3
		170	4.89×10^{-5}				
		140.0 ± 0.02	4.72×10^{-6}				
		(25) ^a	8.23×10^{-12}				
5		160.0 ± 0.02	$(3.15 \pm 0.01) \times 10^{-4}$	13.3	1	27.8	-11.0
		150.0 ± 0.02	$(1.48 \pm 0.02) \times 10^{-4}$				
		140.0 ± 0.02	$(6.29 \pm 0.11) \times 10^{-5}$				
		(25) ^a	8.99×10^{-11}				
6		140.0 ± 0.02	$(7.00 \pm 0.03) \times 10^{-4}$	148	11.1	27.2	-7.8
		130.0 ± 0.02	$(2.67 \pm 0.02) \times 10^{-4}$				
		120.0 ± 0.02	$(1.23 \pm 0.02) \times 10^{-4}$				
		(25) ^a	1.29×10^{-9}				

^a Rates at 25° are extrapolated from higher temperatures.

starting with 7,7-dimethoxy-2,3-dimethylbicyclo[2.2.1]-heptadiene (7).⁵ The monomethylated *p*-nitrobenzoate **5** was prepared from 2-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**12**) which was synthesized *via* the reaction of 2-chlorobicyclo[2.2.1]hept-2-en-*anti*-7-ol (**13**) with excess methyl lithium.⁶

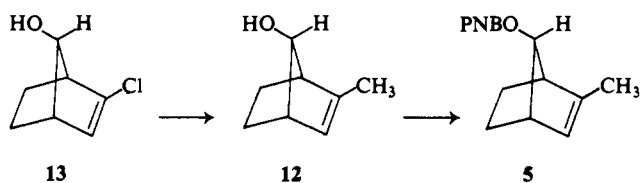
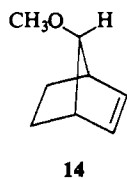


Table I lists the rates of solvolysis of **4**, **5**, and **6** in 70:30 dioxane-water (the rate for **4** at 170 and 185° had previously been measured in 70:30 dioxane-water⁷). We had shown earlier⁸ that the reactions being studied involved alkyl oxygen bond cleavage and not acyl oxygen bond cleavage by demonstrating that the solvolysis of the least reactive member of the series, **4**, in methanol (a solvent very similar to 70:30 dioxane-water in ionizing power) gave only the corresponding methyl ether, **14**, with complete retention of stereochemistry.



Product analysis showed that in 70:30 dioxane-water **5** gave exclusively **12** and **6** gave only **10**. In the case of **5** an 82% yield of **12** was obtained after one half-life

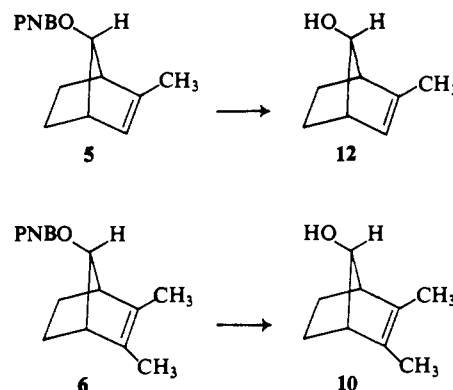
(5) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **90**, 7271 (1968).

(6) A detailed discussion of the reaction of vinyl halides with organolithium reagents will be forthcoming.

(7) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **89**, 1954 (1967); see also H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967). The difficulties encountered in utilizing dioxane as a solvent can be minimized by degassing the solutions prior to sealing in ampoules.

(8) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **91**, 1545 (1969).

based on 50% reaction, while after ten half-lives a 64% yield of **12** was obtained. It was shown that **12** slowly



decomposed under the reaction conditions. In contrast **10** was stable for prolonged periods under the conditions of solvolysis. Thus, **6** gave a 99% yield of **10** after ten half-lives.

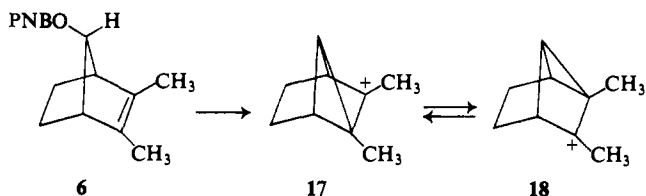
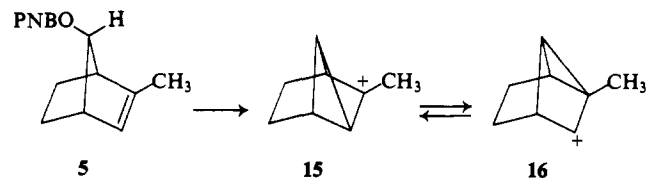
Examination of the rate data listed in Table I shows that at 140° the introduction of one methyl group gave a rate acceleration of 13.3 in comparison to the rate of **4**. The introduction of the second methyl group caused a rate increase of 11.1 for **6** relative to **5**. These rate changes clearly represent a "cumulative" effect of the added methyl groups. If classical equilibrating ions had been formed in the solvolysis of **4**, **5**, and **6**, we would have expected a rate increase in the rate of solvolysis of **5** relative to **4** due to the increased stability of the initially formed tertiary cation **15**. However, since **6** would be expected to give **17**, a tertiary ion very similar to **15**, the second methyl group would be expected to have relatively little effect on the rate of solvolysis of **6** relative to **5** if rapidly equilibrating classical ions were being produced in these solvolyses.

Bartlett and Sargent have discussed in detail the cumulative effect of methyl substitution on solvolysis rates⁹ and have noted several types of reactions,⁹⁻¹¹ all of

(9) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

(10) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931); S. V. Anantkrishnan and C. K. Ingold, *ibid.*, 984, 1396 (1935).

(11) J. Boësen and J. Stuurman, *Rec. Trav. Chim.*, **56**, 1034 (1937); D. Swern, *Chem. Rev.*, **45**, 1 (1949).



which are believed to occur through the intermediacy of symmetrical transition states.⁹⁻¹² In contrast, reactions such as the acid-catalyzed hydration of olefins, which are believed to occur *via* the formation of unsymmetrical, classical carbonium ion intermediates, do not show a cumulative effect of methyl substitution on the rate of reaction. For instance, whereas isobutylene undergoes acid-catalyzed hydration *ca.* 10^3 times faster than propene, 2-methyl-2-butene undergoes hydration slower than isobutylene and *trans*-2-butene undergoes hydration slower than propene.^{9,13} It should be noted that the addition of the methyl group to the other end of the double bond *has a rate-retarding effect* in these reactions.

On the basis of the considerations discussed above we feel that our data on the solvolysis of 4, 5, and 6 are most consistent with the formation of a symmetrical, delocalized 7-norbornenylium cation.

Acknowledgment. The authors are indebted to the Petroleum Research Fund, administered by the American Chemical Society, for a grant which supported this investigation.

(12) See also H. Tanida and H. Ishitobi, *J. Am. Chem. Soc.*, **88**, 3663 (1966); H. Tanida, *Accounts Chem. Res.*, **1**, 238 (1968); P. von R. Schleyer and G. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

(13) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957).

(14) Alfred P. Sloan Research Fellow, 1967-1969.

(15) Goodyear Research Fellow, 1966-1967.

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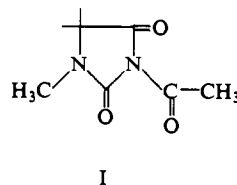
Received January 13, 1969

Selective Neutral Acylations

Sir:

To examine their acylating ability several new cyclic N-acylimides were prepared by standard methods and characterized by analytical and nmr data: 3-acetyl-, 3-benzoyl- and 3-*p*-tosyl-1,5,5-trimethylhydantoin; 1-acetyl-3-methyl- and 1,3-diacetyl-2,4,5-imidazolidinetrione. Acylation experiments of different types of alcohols, phenols, and amines indicated that 3-acetyl-1,5,5-trimethylhydantoin (Ac-TMH; I) is the most promising.

A simple procedure to prepare Ac-TMH is as follows:



a solution of 1,5,5-trimethylhydantoin¹ (0.01 mol) in acetic anhydride (9 ml) is refluxed during 1.5 hr; removal of acetic acid and excess anhydride *in vacuo* followed by crystallization from ethyl acetate-hexane furnishes Ac-TMH (89% yield), mp 126-127°.²

A typical acetylation is: 2-naphthol (0.001 mol) in anhydrous acetonitrile (1 ml) and Ac-TMH (0.001 mol) are heated 12 hr at 80°; removal of the solvent and washing with water³ give in quantitative yield 2-naphthyl acetate, identified by mixture melting point. Other dry solvents (benzonitrile, dioxane, chloroform, benzene, and *t*-butyl alcohol) are also suitable for this reaction.

Competition experiments provided interesting results as illustrated by the following example: 2-naphthol (0.001 mol) and 2-octanol (0.001 mol) were dissolved in benzonitrile (1 ml), Ac-TMH (0.00025 mol) was added, and the solution was heated at 80° for 12 hr; the nmr spectrum showed that the reaction was complete⁴ and that practically only the phenolic acetate (δ 2.33 ppm) was formed. This and similar results suggested that Ac-TMH may be useful for the selective acetylation *under neutral conditions* of the phenolic function in the presence of the alcoholic group.

Reaction of *p*-hydroxybenzyl alcohol with an equimolecular amount of Ac-TMH in acetonitrile at 80° for 12 hr produces, according to nmr measurements, a mixture of the phenolic (91%) and alcoholic (9%) monoacetates and 1,5,5-trimethylhydantoin (100%). Under the same conditions acetic anhydride leads to the phenolic and alcoholic monoacetates and the diacetate derivative in a ratio 3:1:2 and 16% recovery of *p*-hydroxybenzyl alcohol.

The selectivity of Ac-TMH is further illustrated by the monoacetylation of 17 β -estradiol. The nmr spectrum (in CDCl₃) of the crude reaction product washed with water³ shows a sharp peak of the phenolic acetate at δ 2.27 ppm; the absence of absorption in the region at δ 4.7 ppm (H α to an acetoxy group) demonstrates that the alcoholic hydroxyl is not acylated.⁵ Besides, thin-layer chromatography indicates that the crude product is essentially estradiol 3-acetate containing estradiol as an impurity. Column chromatography on Florisil with benzene-acetone mixtures followed by recrystallization from ethyl acetate-hexane affords in 60% yield estradiol 3-acetate, mp 136-139° (lit.⁶ mp 136.5-137.5°).

The nmr spectrum of the mixture from the reaction of

(1) O. O. Orazi, R. A. Corral, and J. D. Bonafede, *Anales Asoc. Quim. Arg.*, **45**, 139 (1957); O. O. Orazi and R. A. Corral, *Experientia*, **21**, 508 (1965).

(2) The Ac-TMH remained unchanged after several months in a desiccator.

(3) Evaporation of the aqueous extract leads to quantitative recovery of 1,5,5-trimethylhydantoin, mp and mmp 161-163°.

(4) It lacks the acetyl group signal (δ 2.65 ppm) of Ac-TMH.

(5) Cf. with the spectrum of estradiol diacetate: N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 1964, p 11.

(6) K. Miescher and C. Scholz, *Helv. Chim. Acta*, **20**, 263 (1937).