II (II → III + IV) are good, the amount of the N-benzyloxycarbonyl peptide which can be bound to the insoluble carrier IIIa is rather low. Finally, it is pertinent to note that we were able to utilize the high molecular weight active esters of N-masked peptides and amino acids described here in the synthesis of linear peptides by their interaction with the suitable amino acid or peptide esters.

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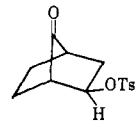
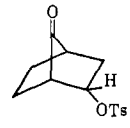
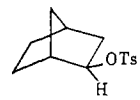
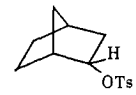
The Solvolysis of 7-Ketonorbornyl Tosylates

Sir:

Much of the attention accorded the solvolysis of various derivatives of bicyclo[2.2.1]heptane[1] has been directed toward establishing the existence[2] or nonexistence[3] of a nonclassical carbonium ion intermediate in the solvolysis of 2-substituted bicyclo[2.2.1]heptanes. Solvolytic results obtained from bicyclo[2.2.1]heptyl tosylates in which the bicyclic system was substituted with groups capable of stabilizing a positive charge (*i.e.*, methyl or phenyl) have been used as evidence both for and against the existence of nonclassical carbonium ions. Since stabilizing the positive charge yields data which are inconclusive, we felt that destabilizing the norbornyl cation might lead to more definitive results.

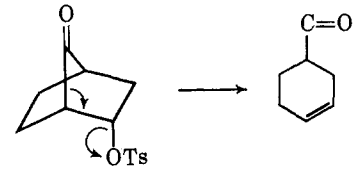
We report here on the effect of the carbonyl function on the acetolysis of 2-*exo*-hydroxybicyclo[2.2.1]heptan-7-one tosylate (**1**) and 2-*endo*-hydroxybicyclo[2.2.1]-heptan-7-one tosylate (**2**).[4,5] The solvolyses of **1** and **2** were carried out in anhydrous acetic acid buffered with sodium acetate at 75, 90, and 100° to yield the specific rate constants listed in Table I.[6] To our knowledge this is the first case of an *endo*-tosylate solvolyzing faster than the *exo* epimer. We envisage three possible rationalizations of this unique *exo/endo* rate ratio: (1) the *exo* and *endo* isomers are solvolyzing by different mechanisms,[7] (2) an unprecedented dipole–dipole interaction is occurring which either accelerates the *endo* solvolysis or inhibits the *exo* solvolysis by a factor $>10^3$,[8] (3) the *exo*-tosylate, **1**, is solvolyzing without anchimeric assistance while all other known *exo*-norbornyl tosylates solvolyze with anchimeric assistance. This latter rationalization appears to be the most attractive.[7,8]

Table I. Acetolysis Rates of Various Norbornyl Tosylates

Compound	Ref.	Temp., °C.	Rate, sec.$^{-1}$	ΔH^*, kcal./mole	ΔS^* e.u.
 1		100.00	(1.84 ± 0.01) × 10^{-4} [a]	27.1	−3.5
		90.00	(5.96 ± 0.06) × 10^{-5}		
		75.71	(1.33 ± 0.01) × 10^{-5}		
		(25.0)	1.44 ± 10^{-8}		
 2		100.00	(4.66 ± 0.00) × 10^{-4}		
		90.00	(1.79 ± 0.03) × 10^{-4}	24.7	−8.1
		75.74	4.28 × 10^{-5}		
		(25.0)	8.66 × 10^{-8}		
	6	25	2.33 × 10^{-6}	21.6	−7.2
	6	(25)	8.28 × 10^{-8}	25.8	−4.4

[a] A similar rate for solvolysis of the *exo*-tosylate has been obtained by K. Mislow and W. Meyer. For details see W. E. Meyer, Ph. D. thesis, New York University, 1964.

In considering the large *exo/endo* rate ratio which is generally observed in the solvolysis of norbornyl tosylates, the two published explanations[1,2,9–11] of this phenomenon require evaluation. According to both **1** and **2** yield products with the 7-ketonorbornane skeleton intact, this rationalization is ruled out. A discussion of the product analysis of **1** and **2** will be published in the near future.



(1) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 111.

(2) For a leading reference see S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

(3) For a leading reference see H. C. Brown and M. H. Rei, *ibid.*, **86**, 5008 (1964).

(4) The *exo*-tosylate, **1**, was synthesized from 7,7-dimethoxybicyclo-[2.2.1]heptene *via* a four-step synthesis consisting of epoxidation, lithium aluminum hydride reduction, hydrolysis, and reaction with *p*-toluenesulfonyl chloride. The isomer **2** was prepared from 7,7-dimethoxybicyclo[2.2.1]heptan-*exo*-2-ol *via* oxidation, Meerwein–Ponndorf–Verley reduction, hydrolysis, and reaction with *p*-toluenesulfonyl chloride. The stereochemistry of the epimeric 7,7-dimethoxybicyclo-[2.2.1]heptan-2-ols was established by n.m.r., near-infrared hydrogen bonding studies, and chemical conversion to known compounds.

(5) Correct analytical data have been obtained for all new compounds named with the exception of **2**. This tosylate could not be obtained in greater than 90% purity. Thus the acetolysis rates on **2** are based on infinity titers of *ca.* 90%.

(6) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965). It must be stressed at this point that comparison of the absolute rates of solvolyses of the 7-keto compounds with other absolute rate constants is complicated by the inductive effect of the carbonyl and the change in geometry of the system which results from the incorporation of the carbonyl in the 7 position.

(7) (a) The possibility that the rate of solvolysis of **2** is accelerated by hemiacetal formation followed by an intramolecular SN2 displacement requires consideration. Solvent interactions of this type could occur. However, *if* this type of internal displacement was responsible for an acceleration of the solvolysis of **2** by a factor of 10^2–10^3, changing solvent should produce a drastic change in the absolute rate of solvolysis of **2** and in the *exo/endo* rate ratio. In fact, ethanolysis of **1** and **2** gave rates which were very close to the acetolysis rates both in absolute rate values and in the *exo/endo* rate ratio of 2.1 (at 100°) *vs.* 0.4 (at 100°) for acetolysis. (b) A concerted bond cleavage process leading to an acyl carbonium ion is an alternate mechanism for the solvolysis of **2**. Since both **1** and **2** yield products with the 7-ketonorbornane skeleton intact, this rationalization is ruled out. A discussion of the product analysis of **1** and **2** will be published in the near future.

(8) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **86**, 1161 (1964), have shown that not only the presence of an inductive group, but also its orientation relative to the reaction site, can influence solvolysis rates. The orientation factors studied by these workers generally changed the rates by a factor of less than ten. In comparing our rates with those of the epimeric norbornyl tosylates we find a change in the *exo/endo* rate ratio of 1.7 × 10^3. We doubt that an orientation factor could be that large; however, we cannot unequivocally rule out this possibility. Experiments are in progress to determine the orientation effect of the carbonyl group on solvolyses rates in rigid systems.

(9) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962.

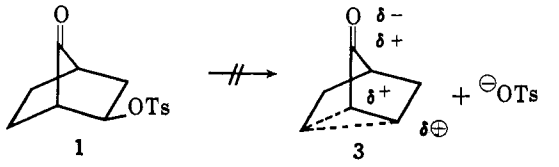
(10) H. C. Brown, F. J. Chloupek, and M. H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(11) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

one postulate the norbornyl cation exists as a rapidly equilibrating pair of classical ions,[9,10] with both *exo*- and *endo*-norbornyl tosylates undergoing initial ionization to a classical cation. The fact that the *exo* isomer solvolyses 10^2–10^3 times faster than the *endo* isomer has been rationalized by the hypothesis that the *endo* isomer is abnormally slow due to steric hindrance to ionization of the *endo*-tosylate in the 2 position by the *endo*-hydrogen in the 6 position.[9,10] The alternate hypothesis is that the large *exo*/*endo* rate ratio observed for the solvolyses of norbornyl tosylates is due to anchimeric assistance by the 1–6 σ electrons in the solvolysis of the *exo* isomer.[1,2,11]

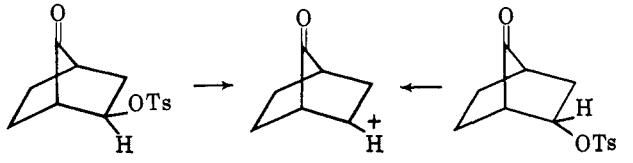
If both *exo*- and *endo*-norbornyl tosylates initially solvolyze to the same classical carbonium ion, the presence of a carbonyl function in the 7 position should have relatively little effect on the inhibition of solvolysis by the C-6 *endo*-hydrogen. Thus the *exo*/*endo* rate ratio for **1** and **2** should be 10^2–10^3 barring other effects.[8]

Alternatively, if the norbornyl *exo*/*endo* rate ratio is due to anchimeric assistance, the presence of a carbonyl function at C-7 would be expected to have drastic effects. The solvolysis of **1** should lack the rate enhancement characteristic of tosylate displacements which occur with neighboring participation because



1 **3**

the accumulation of positive charges in the transition state leading to **3** would be expected to inhibit the formation of a delocalized structure. Thus **1** would be expected to solvolyze to the classical ion, **4**. It is assumed that the *endo*-tosylate, **2**, would also solvolyze to a



1 **4** **2**

classical ion,[7,8] since it is commonly agreed upon that *endo*-norbornyl arenesulfonates solvolyze in the rate-determining step to classical ions.[1,2,9–13] If the large *exo*/*endo* rate ratio observed in the norbornyl tosylate solvolyses is due to anchimeric assistance, **1** and **2** should solvolyze with an *exo*/*endo* rate ratio of approximately 1 since anchimeric assistance would be inhibited by the presence of the carbonyl function.

The fact that **1** solvolyses 6.0 times slower (at 25°) than **2** appears to be most consistent with nonclassical carbonium ion theory. The factor of 6.0 is in amazingly good agreement with the calculations of Schleyer, who predicted[14] that the C-6 *endo*-hydrogen, rather than slowing the rate of solvolysis of the *endo*-tosylate, would actually accelerate the rate by a factor of five due to nonbonded interactions with the tosylate functions.

(12) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).
(13) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).
(14) P. von R. Schleyer, Symposium on Linear Free Energy Correlation, Durham, N. C., Oct. 19–21, 1964, Preprints of Papers, p. 225.

Acknowledgment. The authors are indebted to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work. We also wish to thank Professor Kurt Mislow for informing us of his results and for helpful discussions of this problem.

(15) National Science Foundation Cooperative Predoctoral Fellow, 1962–1963, 1964–1965.

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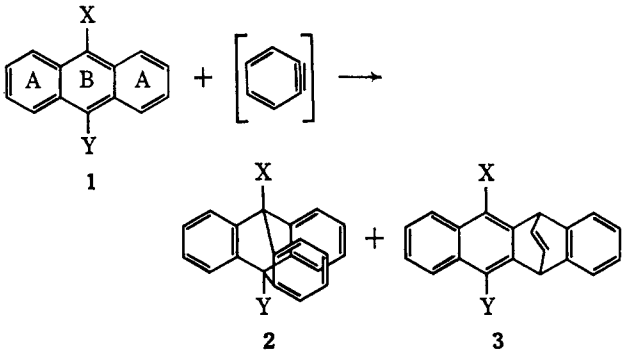
Received June 14, 1965

Novel Products from the Reaction of Benzyne with Anthracenes

Sir:

Benzyne reacts with anthracene (**1a**) to produce triptycene (**2a**)[1] and is thereby reacting in a Diels–Alder manner with the more reactive **B** ring of the anthracene molecule. We have found that benzyne also reacts in Diels–Alder fashion with the A ring of anthracene and that the relative amounts of A-ring and B-ring addition products can be modified by substituents appended to the anthracene system.



1 **2** **3**

1a, X = Y = H
b, X = CN, Y = H
c, X = Y = CN
d, X = Y = C_6H_5

Benzyne was generated from anthranilic acid diazotized *in situ* by the procedure of Friedman and Logullo[1f] and condensed with anthracene (**1a**), 9-anthronitrile (**1b**), and 9,10-anthracenedicarbonitrile (**1c**) to give A-ring adducts (**3**) and B-ring adducts (**2**) as well as recovered starting material. Table I shows the results which were obtained by vapor-phase chromatographic analyses of the reaction mixtures.

The A-ring and B-ring adducts were isolated from larger-scale reactions (20–50 g. of the appropriate anthracene) by column chromatography (Florisil and/or neutralized alumina) and crystallization techniques. The B-ring adducts (9-X, 10-Y-triptycenes) were identified by their spectral properties, especially their ultraviolet and n.m.r. spectra, as recorded in Table II. The ultraviolet spectra showed only nonconjugated phenyl absorption, and the n.m.r. spectra were sym-

(1) (a) G. Wittig and R. Ludwig, *Angew. Chem.*, **68**, 40 (1956); (b) G. Wittig, *Org. Syn.*, **39**, 75 (1959); (c) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); (d) E. LeGoff, *ibid.*, **84**, 3786 (1962); (e) G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95**, 2718 (1962); (f) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963); (g) M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963); (h) H. Günther, *Chem. Ber.*, **96**, 1801 (1963).