Tetrahedron Letters No. 7, pp 663 -666 , 1978. Pergamon Press. Printed in Great Britain.

# INDUCTIVE AND HYPERCONJUGATIVE EFFECTS IN THE SOLVOLYSIS OF 4-SUBSTITUTED BICYCLO[2.2.2]OCT-1-YL p-NITROBENZENESULFONATES

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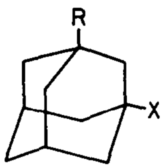
(Received in UK 12 December 1977; accepted for publication 28 December 1977)

As previously reported [1] the solvolysis rates of 1-R substituted 3-bromoadamantanes (1), X = Br, in 80 % ethanol correlate well with the inductive substituent constants $\sigma_I^q$ of alkyl and electron withdrawing groups, as derived from the $pK_a$ values of 4-substituted quinuclidinium perchlorates 2 [2]. In cases where R was a +M substituent, such as OH, $OCH_3$, $SCH_3$, $C_6H_5$, or an electrofugal group [3], such as $Sn(CH_3)_3$, $COO^-$, $CH_2OH$, $CH_2NH_2$ or $CONH_2$, solvolysis to alcohols 1, X = OH, and ethers 1, X = OEt, occurred 2.5 to 44 times as fast as calculated from the $\sigma_I^q$ values of these substituents. This acceleration was ascribed to hyperconjugative delocalization of the positive charge in the transition state for ionization 3. Only when strong +M substituents such as $(CH_3)_2N$, $O^-$ and $S^-$ were present at C(1) did concerted fragmentation [4] to products of type 4, where R = $(CH_3)_2N^+$, O and S, take place.



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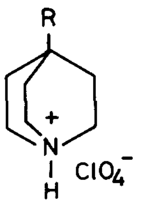

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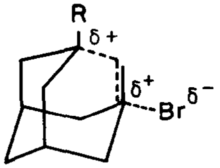

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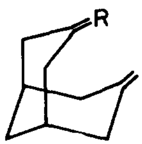

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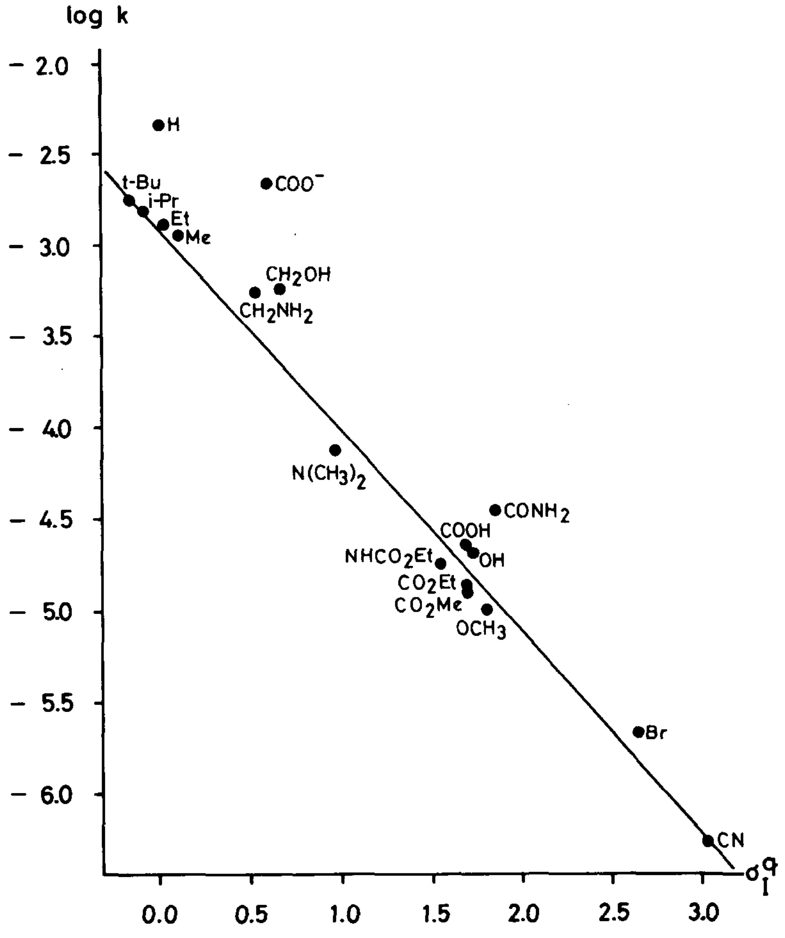
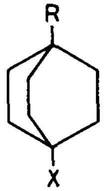
Table. First order rate constants for 4-R-bicyclo[2.2.2]octyl p-nitrobenzenesulfonates in 80 vol. % ethanol at 75° C.

| R | k x $10^5$ ($s^{-1}$) |
|---|---|
| a) H | 462 |
| b) $COO^-$ | 219 |
| c) t-Bu | 185 |
| d) i-Pr | 153 |
| e) Et | 130 |
| f) Me | 114 |
| g) $CH_2OH$ | 56.2 |
| h) $CH_2NH_2$ | 54.6 |
| i) $N(CH_3)_2$ | 7.40 |
| j) $CONH_2$ | 3.56 |
| k) COOH | 2.32 |
| l) OH | 2.12 |
| m) $NHCOOC_2H_5$ | 1.80 |
| n) $COOC_2H_5$ | 1.37 |
| o) $COOCH_3$ | 1.26 |
| p) $OCH_3$ | 1.02 |
| q) Br | 0.218 |
| r) CN | 0.054 |

Figure. Plot of log k for 4-R-bicyclo[2.2.2]octyl p-nitrobenzenesulfonates against $\sigma_I^q$.

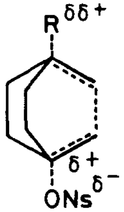


Hyperconjugation involving a single CC-bond as well as fragmentation are precluded when the electron donor and the positive reaction center are separated by an additional carbon atom, as in 4-R-bicyclo[2.2.2]octyl p-nitrobenzenesulfonates (nisylates) (5). The solvolysis rates of the latter compounds should therefore be controlled by the inductive effect of *R* alone, unless ionization is assisted by twofold hyperconjugation, as illustrated in 7. Such extended σ-bond delocalization (depicted for only one of the three ethano bridges in 7) has not been observed before and is in accordance with the principle of ethylogy [5]



5 X = p-$NO_2C_6H_4SO_3$

6 X = OH



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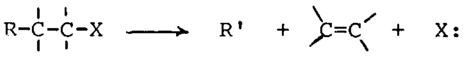
Hydrolysis of 18 nisylates 5 (Table) in 70 % dioxane yielded only the respective alcohols 6. The rate constants for these compounds in 80 vol. % ethanol cover a range of 8.5 x $10^3$ (Table), and their logarithms correlate well with the inductive constants $\sigma_I^q$ of the 4-substituents, except in the cases where R = H, $COO^-$, $CONH_2$, $CH_2OH$ and $CH_2NH_2$ (Figure). These compounds reacted 3.7, 7.7, 3.1, 2.4 and 1.7 times, respectively, faster than anticipated on the basis of substituent $\sigma_I^q$ values. These accelerations are well beyond the maximum deviation from the regression line defined by the other substituents, i.e. ± 40 %. The common feature of the above substituents and of hydrogen is that they are potentially electrofugal [3], i.e. they are released without the bonding electron pair in heterolytic fragmentation and 1,2-elimination of the type:



$$R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \longrightarrow R' + >C=C< + X:$$

where R' is $CO_2$, HNCO, $CH_2=O$, $CH_2=NH_2^+$ and $H^+$, respectively. These substituents appear to assist the ionization, albeit weakly, of nisylates 5 by twofold CC- or by CH-CC-hyperconjugation, respectively, as illustrated in 7.

It is noteworthy that the alkyl groups follow the inductive order Me < Et < i-Pr < t-Bu and that they are all less electron-releasing than hydrogen (Table). In their earlier study of the acetolysis rates of the p-bromobenzenesulfonates of several 4-substituted bicyclo[2.2.2]octanols 6 Schleyer and Woodworth[6] observed the anomalous position of hydrogen relative to alkyl. However, they ascribed this to a change in skeletal geometry attending the replacement of hydrogen by the bulkier alkyl groups. The present study of a wider range of 4-substituents suggests twofold hyperconjugation as a plausible alternative.

## REFERENCES

1) C.A. Grob, W. Fischer & H. Katayama, Tetrahedron Letters 1976, 2183; C.A. Grob, Angewandte Chemie, internat. edit. 15, 569 (1976).

2) C.A. Grob & M.G. Schlageter, Helv. chim. acta 59, 264 (1976).

3) C.A. Grob & P.W. Schiess, Angewandte Chemie, internat. edit. 6, 1 (1967).

4) C.A. Grob, ibid. 8, 535 (1969).

5) C.A. Grob, Experientia 13, 126 (1957).

6) P. von R. Schleyer & C.W. Woodworth, J. Am. Chem. Soc. 90, 6528 (1968).