

NEIGHBORING GROUP PARTICIPATION BY A "TWISTED" DOUBLE BOND<sup>1</sup>

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Neighboring group participation by the carbon-carbon double bond in solvolysis reactions has been an extensively studied and much discussed subject. Perhaps the best known example of this phenomenon is the neighboring group participation of the double bond of **1**, whose interaction with the incipient carbonium ion center is manifest in an anchimeric assistance of 10<sup>11</sup> (rate acceleration) relative to **2**.<sup>3</sup> Studies have shown that this participation occurs through

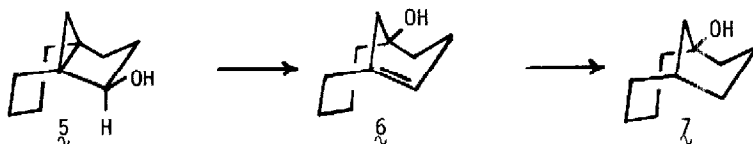


*symmetrical* stabilization of the developing positive charge by the carbon-carbon double bond.<sup>3,4</sup> When the double bond is less well situated for through space stabilization, an inductive retardation of rate is often noted.<sup>5</sup> For instance, **3** solvolyzes *ca.* 0.8 times as fast as **4**, indicating a net inductive destabilization of the incipient cation. In view of the extensive data



available on the double bond as a participating group, we felt that it would be of interest to similarly evaluate "twisted" carbon-carbon double bonds.<sup>6</sup> We now wish to report what we believe to be the first example of neighboring group participation by a "twisted, Bredt's rule type" double bond.

Acid-catalyzed rearrangement of **5** gave a mixture of products from which **6** could be isolated in 36% yield.<sup>7</sup> Catalytic reduction of **6** over 5% palladium on carbon gave a 97% yield of **7**. Treatment of **6** and **7** with *n*-butyllithium followed by the addition of *p*-nitrobenzoyl chloride gave the *p*-nitrobenzoate esters **8** and **9**, respectively.<sup>8</sup> Solvolysis of **8** and **9** was carried out in 70:30 v/v acetone/water. Table I lists the rates of solvolysis of these *p*-nitrobenzoates. As can be seen from the data in Table I, the presence of the double bond in **8**



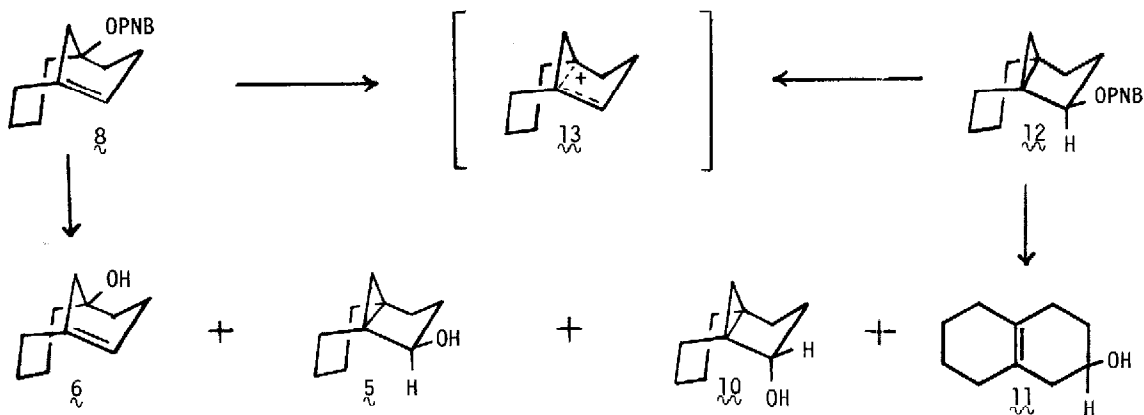
resulted in a rate acceleration of 120. That this rate acceleration was a result of neighboring group participation and not of some other factor was supported by product studies. Analysis of the product mixture showed that the product ratio changed with time. After 10 half-lives, **8** gave 62% of **6**, 12% of **5**, 8% of **10**, and 6% of **11**. This can be compared with the

Table I. Rates of Solvolysis of *p*-Nitrobenzoates of Bicyclo[4.3.1]dec-6-en-1-ol and Bicyclo[4.3.1]decan-1-ol in 70:30 v/v Acetone/Water.

Compound	Temp. ( $\pm 0.02^\circ\text{C}$ )	Rate ( $\text{sec}^{-1}$ )	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)
	85.00	$(5.29 \pm 0.22) \times 10^{-4}$	24.9 $\pm$ 0.5	-4.2 $\pm$ 1.4
	70.00	$(1.19 \pm 0.03) \times 10^{-4}$		
	55.00	$(1.97 \pm 0.05) \times 10^{-5}$		
	25.00 <sup>a</sup>	$3.84 \times 10^{-7}$		
	129.80	$(8.26 \pm 0.01) \times 10^{-4}$	27.7 $\pm$ 0.4	-4.5 $\pm$ 1.1
	115.10	$(2.29 \pm 0.05) \times 10^{-4}$		
	99.90	$(4.79 \pm 0.10) \times 10^{-5}$		
	25.00 <sup>a</sup>	$3.20 \times 10^{-9}$		

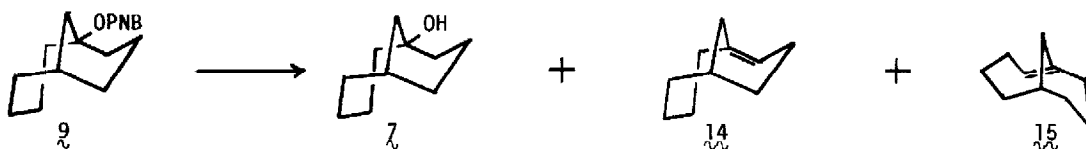
a) Extrapolated from higher temperatures.

solvolysis of **12**, which gave 59% of **6**, 5% of **5**, 7% of **10**, and 20% of **11** after 10 half-lives.<sup>7</sup> After 10% reaction, only trace amounts of **11** could be detected from the solvolysis of **8**. This



indicated that  $\underline{11}$  was a secondary product. The close similarities between the product mixtures obtained from  $\underline{8}$  and  $\underline{12}$  indicated that both of these *p*-nitrobenzoates were probably undergoing ionization to yield primarily<sup>9</sup> the same cationic intermediate,  $\underline{13}$ . The formation of both  $\underline{5}$  and  $\underline{10}$  clearly requires interaction of the incipient cationic center with the "twisted" double bond of  $\underline{8}$ .

The solvolysis of  $\underline{9}$  gave a mixture of  $\underline{7}$ ,  $\underline{14}$ , and  $\underline{15}$ . The ratio of these products changed with time due to the slow conversion of both  $\underline{14}$  and  $\underline{15}$  into  $\underline{7}$  under the reaction conditions. While the ratio of  $\underline{7}:\underline{14}:\underline{15}$  was 82:10:8 after five half-lives, it was 92:7:1 after twenty half-lives. The structure of  $\underline{7}$  was established through comparison with starting material. The



structures of  $\underline{14}$  and  $\underline{15}$  were assigned on the basis of infrared spectral data, nuclear magnetic resonance spectral data, and exact mass molecular weight.<sup>10</sup> The olefin  $\underline{14}$  showed the following physical properties: exact mass observed,  $m/e$  136.1253 (calcd.  $m/e$  136.1252); nmr ( $CCl_4$ )  $\delta$  1.13 - 2.57 (complex multiplet, 15 H), 5.55 (t,  $J = 5.5$  Hz, 1H); ir ( $CCl_4$ ) 3025, 1650  $cm^{-1}$ . This data can be compared with that of  $\underline{6}$ , which showed one olefinic proton in the nmr at  $\delta$  5.54 with a coupling constant of 5.5 Hz and a C=C stretching absorption at 1652  $cm^{-1}$ . The olefin  $\underline{15}$  showed: exact mass observed,  $m/e$  136.1251 (calcd.  $m/e$  136.1252); nmr ( $CCl_4$ )  $\delta$  1.17 - 2.70 (broad multiplet, 15 H), 5.27 (t,  $J = 6$  Hz, 1 H); ir ( $CCl_4$ ) 3030, 1661  $cm^{-1}$ . These data can be compared with those of bicyclo[4.2.1]non-1-ene, which showed<sup>6</sup> one olefinic proton in the nmr at  $\delta$  5.30 with a coupling constant of 7 Hz and a C=C stretching absorption at 1655  $cm^{-1}$ .

In order to insure that the solvolysis of  $\underline{9}$  involved alkyl-oxygen bond fission and not just an acyl-oxygen hydrolysis reaction, the solvolysis was carried out in 23% oxygen-18 labelled water. Mass spectral analysis showed that the isolated alcohol contained  $20 \pm 1\%$  oxygen-18. Thus, alkyl-oxygen cleavage was clearly involved in the solvolysis of  $\underline{9}$ .<sup>11</sup>

In summary, we have established that a "twisted" double bond can behave as a rate-accelerating neighboring group. The rate acceleration observed for  $\underline{8}$  relative to  $\underline{9}$ , coupled with the rate deceleration of  $\underline{3}$  relative to  $\underline{4}$ , provides some estimate of the size of this effect.

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8. Satisfactory elemental analyses were obtained on all new compounds unless otherwise specified. Spectral data were consistent with the assigned structures in all cases.
9. The qualifying term "primarily" is used here because the three major primary products are slowly converted into 11. This implies the presence of an alternate, very minor, mechanistic path.
10. Because of the extremely small quantities of 14 and 15 which were available, classical elemental analyses were not obtained.
11. The small difference in <sup>18</sup>O content between the solvent and the isolated alcohol was probably due to a small amount of exchange between the water and the acetone during the course of the reaction. Because of the very small difference involved, no attempt was made to unequivocally establish this point.