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SOLVOLYSIS OF EXO-TETRACYCLO[4.4.0.0^{2,4}.0^{3,9}]DEC-10-YL DERIVATIVES; AN EXTREMELY REACTIVE TRISHOMOCYCLOPROPENYL SYSTEM[1]

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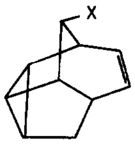
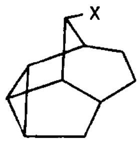
Recently we reported[2] that acid cleavage of exo-10-t-butoxytetracyclo[4.4.0.0^{2,4}.0^{3,9}]-dec-7-ene (Id)[3] yielded exo-2-acetoxytetracyclo[4.3.1.0^{3,8}.0^{7,9}]dec-4-ene (IIIe) probably via the trishomocyclopropenyl cation V. We now present the results of a study of the hydrolyses of the 3,5-dinitrobenzoates Ia and IIa[4].



I



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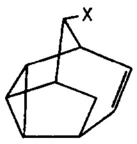

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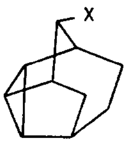
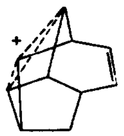


IV

a: X = ODNB
b: X = OH
c: X = OTs
d: X = O-t-Bu
e: X = OAc



V

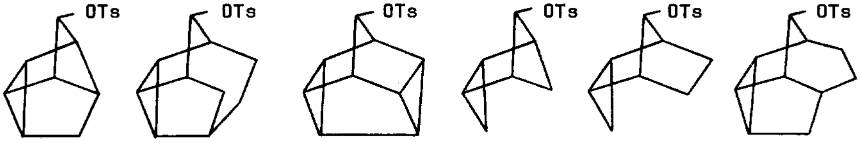
In 60/40 (v/v) acetone-water and in the presence of a slight excess of 2,6-lutidine Ia and IIa gave IIIb (75%) and IVb (80%) besides the products of internal return IIIa and IVa, respectively[5]. Ib and IIb could not be detected by GLC (detection limit 1% in the presence of 99% of rearranged material) and control experiments showed that both Ib and IIb were stable under the hydrolysis conditions. Kinetic data for hydrolysis of Ia and IIa are summarized in table 1. Ia liberated 76 - 82% 3,5-dinitrobenzoic acid and IIa 85 - 90%. After correction for internal return[6] good first order behaviour obtained.

Table 1. Rates of hydrolysis of Ia and IIa in 60/40 (v/v) acetone-water

	k_{100} sec$^{-1\,a}$	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ (e.u.)
Ia^{b}	4.93×10^{-4}	26.2 ± 0.4	- 3.9 ± 1.2
IIa^{c}	5.74×10^{-3}	23.7 ± 0.3	- 5.7 ± 0.9

a. Values obtained by extrapolation from lower temperatures,
b. Studied by the ampoules technique,
c. Studied at constant pH = 7 by continuous titration[7].

If it is assumed that the same ratio $\frac{k_{\text{ROTs (acetic acid, 25°)}}}{k_{\text{RODNB (acetone-water, 60/40, 100°)}}} \approx 450$ applies to the reactions of Ia and IIa as it does to other systems[8] the rates of acetolysis (25^{o}) of the hypothetical tosylates Ic and IIc must be 2.2×10^{-1} sec^{-1} and 2.6 sec^{-1}, respectively. Both systems then belong to the most reactive homocyclopropylcarbinyl systems known today:



$\lg \frac{k}{k_{7\text{-norbornyl}}}$	10	11	12	13	14	14-15

Since IIIb and IVb were also obtained as the sole products of the hydrolyses of IIIc[9], IVa[1a], and IVc[9] we assume that V and V-H_2 are formed from III and IV-type materials, too.[9] From the rates of hydrolysis of IVa ($k_{100} = 5.39 \times 10^{-6}$ sec^{-1})[1a] and of IIa, $R = \frac{k_{IIa}}{k_{IVa}} = 1065$, and from the minimum product ratio $P = \frac{[IVb]}{[IIb]} = 100$, we calculate[10] a difference in ground state free energies (at 100^{o}) between II-X and IV-X, $\Delta F = 2.3\ RT\ \lg RP = 8.6$ kcal/mole. Thus, besides the favorable interaction between cyclopropane ring and developing charge, relief of ground state strain is responsible for the high reactivity of systems I and II.

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b. Reported at the IInd IUPAC Conference on Physical Organic Chemistry, Noordwijkerhout, The Netherlands, April 1974.

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