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KINETICS OF REACTIONS IN SOLUTIONS UNDER PRESSURE. XXIV.[1]
THE BASE PROMOTED REACTION OF 3-(*p*-HYDROXYPHENYL)PROPYL BROSYLATE

W. le Noble
Department of Chemistry
State University of New York at Stony Brook, Stony Brook, New York 11790

and

B. Gabrielsen
Department of Chemistry
Wagner College, Staten Island, New York 10301

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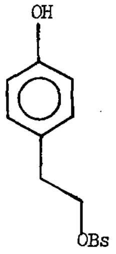
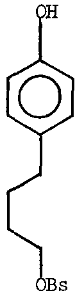
We wish to present evidence that $\mathrm{Ar}_1^{\ominus}$ participation, which leads to spirodienones in the base promoted solvolyses of *ω*-(*p*-hydroxyphenyl)ethyl[2] (I) and -butyl[3] (II) esters, is absent in the solvolysis of the propyl homolog. Presumably the combination of strain in the incipient spiro intermediate and the remoteness of the neighboring group is enough to render such participation ineffective.

In I and II, $\mathrm{Ar}_1^{\ominus}$ participation gives rise to rate increases of 10^6 and of at least 50, respectively. Since such participation is likely to decrease not only as the number of intervening carbon atoms is raised, but also as the ring strain in the incipient spiro intermediate increases, we considered it of interest to study the behavior of 3-(*p*-hydroxyphenyl)propyl brosylate (III) in *i*-propyl alcohol containing one equivalent of potassium *i*-propoxide. We had previously shown[4] that the small effect of hydrostatic pressure on the rate constants of solvolysis of I and II readily distinguishes these reactions from solvolyses - such as that of 4-*p*-anisylbutyl brosylate (IV) - in which a carbonium ion center must develop, and accordingly we planned to attack the present problem in the same way. The preparation of III involved LAH reduction of *p*-hydroxydihydrocinnamic acid and conversion to the brosylate in the usual way;[5] m.p. 73.5-74.5°; *anal.*, calc.: C, 48.53, H, 4.07, Br, 21.52 and S, 8.64; fd.: C, 48.47, H, 3.95, Br, 21.35 and S, 8.44;

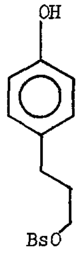
nmr: τ 2.33 (s, 4H), 3.20 (q, 4H), 5.96 (t, 3H, J= 6.1 Hz), 7.44 (t, 3H, J= 7.0 Hz), 8.13 (quintet, 3H). For comparison, 3-phenylpropyl brosylate[6] (V) was also prepared. The reactions were carried out in *i*-propyl alcohol at 35.00°, and the analytical procedures used were the same as before.[4]



I

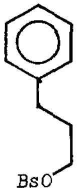


II



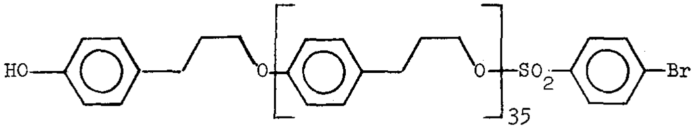
III

IV



V

In neutral *i*-propanol III and V have first order rate constants of (3.9 ± 0.2) and (3.7 ± 0.2) x 10^{-7} sec^{-1}, respectively; the hydroxy group provides virtually no assistance in this reaction. In basic *i*-propanol, III (in 0.02 M concentration) decomposed roughly a hundred times more rapidly, giving rise to almost quantitative yields of potassium brosylate. A polymer (VI) also precipitated in high yield; it could not be melted, was insoluble in all common solvents and had an elemental composition indicating a chain of about 35 $-(O-C_6H_4-CH_2CH_2CH_2-)-$ units (VI)



VI

and the presence of potassium in about 10% of the phenolic end groups; *anal.*, calc.:[7] C, 78.14, H, 7.23, Br, 1.70, K, 0.08, S, 0.68; fd.: C, 77.03, H, 7.51, Br, 1.70, K, 0.08, S, 0.65. The nmr spectrum, measured in diphenyl ether solution at 175°

showed that the CH_2O triplet had moved up by about 0.2 ppm; the other methylene absorptions were relatively unaffected. No i-propyl ether product could be found at all.

It may be recalled that Baird and Winstein had also obtained polymeric products from I under certain conditions.[2] However, it soon became clear that at least part of the product had been obtained via bimolecular displacement reactions. Thus, first order rate plots were strongly curved downward, and dilution depressed the rates considerably (Figure 1). On the other hand, second order rate plots revealed some upward curvature, but this is not due to a first order component since in these plots there is no dilution effect. Excess base also had no effect. The initial value of k_2 is 1.80 x 10^{-3} ^{1}/mole, sec.

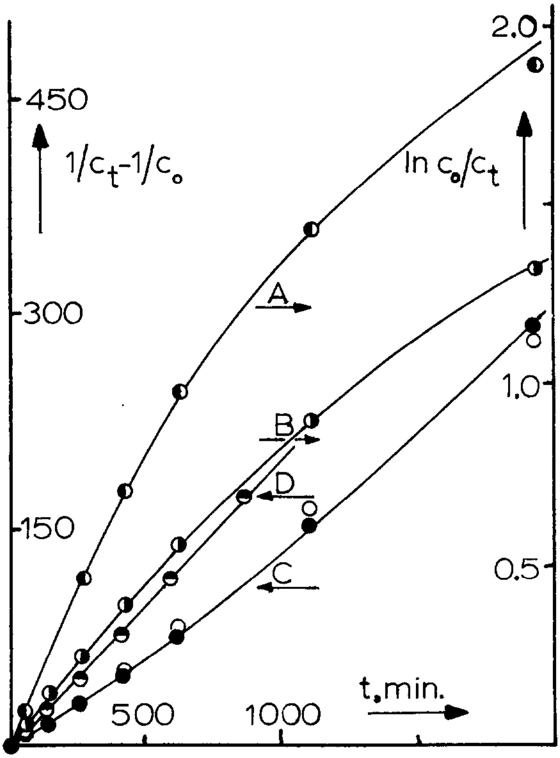


Figure 1 - Rate plots for the reactions in basic i-propanol at 25.00°: (A) III, initial concentration = 0.02 M, first order; (B) same as (A) at 0.01 M; (C) same data as (A) and (B), second order; (D) p-cresoxide, second order, each point at both 0.01 and 0.02 M.

The model reaction of p-cresoxide with V in i-propanol at 35.00° was found to give p-cresyl 3-phenylpropyl ether, b.p. of 205° at 25 mm, n_D^{25} = 1.5520; anal., calc.: C, 84.92, H, 8.02; fd.: C, 85.04, H, 8.13; the nmr spectrum exhibited 1:2:1 triplets centered at 6.22 and 7.27 τ in addition to the other signals expected for this structure. The value of k_2 is 3.25 x 10^{-3} ^{1}/mole, sec. We believe that the somewhat slower rate of the anion of III is due to the fact that this reaction requires the mutual approach of two anions. As the reaction progresses and polymeric materials form, the proximity required of the two anionic centers is not as great, and k_2 eventually approaches the value of that of the model reaction: at 65% reaction, the instantaneous value is 3.1 x 10^{-3} ^{1}/mole, sec.

Both reactions have activation volumes (calculated from 6 initial rate constants over a 4 kbar range) expected[8] for simple ionic displacement: -6.7 ± 1 cm^3/mole for III and -7.5 ± 1 cm^3/mole for the model reaction.

Labeling experiments further show that VI is formed exclusively by displacement and that no symmetrical dienones are present as in the reactions of I and II. LAD reduction of methyl p-hydroxydihydrocinnamate[9] gave deuterium labeled III the nmr spectrum of which was the same as that of III except that the $\mathrm{BsOCH_2}$- triplet was absent. The polymer derived from d_2-III had an nmr spectrum showing that the deuterium atoms had remained exclusively at the positions γ to the rings. We conclude that $\mathrm{Ar}_1^{\ominus}$-4 participation is ineffective compared to the $\mathrm{Ar}_1^{\ominus}$-3 and -5 types, and that solvolysis so assisted cannot compete with displacement. Thus, this reaction joins a number of others in which four-membered rings are more difficult to form than either the three- or five-membered homologs.

Acknowledgement:

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