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DIRECTION OF CLEAVAGE OF PRIMARY OZONIDES FROM p-SUBSTITUTED PROPENYLBENZENES

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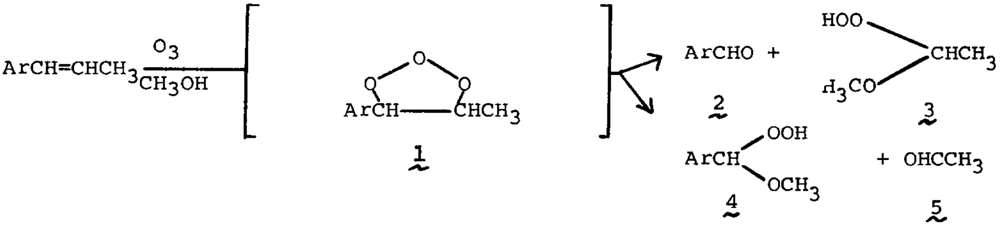
Recent research into the direction of cleavage of primary ozonides resulting from methanolic ozonolysis of alkenylbenzenes has brought out two salient points: a) the proportion of aromatic aldehyde thus directly generated from a series of ring-substituted styrenes was in excellent agreement with the Hammett equation (1), and b) the β-methylated homologs of styrene gave a strikingly larger proportion of benzaldehyde than did styrene itself (2). A logical extension of this work was to study the ozonolysis of a number of ring-substituted propenylbenzenes and ascertain whether or not a free-energy relationship correlated the results.



Early experiments revealed that the workup routine used successfully where Ar was phenyl (2), was not generally applicable with other aryl groups. For example, α, p-dimethoxybenzyl hydroperoxide (4, Ar = p-anisyl) was hydrolyzed to anisaldehyde at a significant rate merely by shaking with water for a couple of minutes at ambient temperature. The contrast of this finding with the integrity of α-methoxybenzyl hydroperoxide (4, Ar = phenyl) toward the same manipulation can be explained through the greater stabilization of an electron-deficient transition stage for hydrolysis by anisyl than by phenyl (3,4).

Our intent then became to seek alternate schemes for determining 2-4, not involving direct isolation. Previous work (2) had indicated that the nmr chemical shifts of the hydroperoxy protons of 3 and 4 and the formyl proton of 2 are sufficiently deshielded ($\delta > 9$ ppm in CCl_4 relative to TMS) such that their signals should be clearly observable in methanol solution. Thus, ozonolysis of styrene and propenylbenzene in CH_3OH was performed at -60 to -65° (2), samples withdrawn at 0°, and the spectrum scanned at this temperature through 800-300 cps. Three reasonably sharp downfield singlets were observed, corresponding to the anticipated signals from 2 and 4 (Ar = phenyl) and the aliphatic hydroperoxide. The product ratios obtained from signal integration were in excellent agreement with the previously determined values (2): See Table I.

TABLE I

OZONOLYSIS OF STYRENE AND PROPENYLBENZENE

STYRENE			
Product	δ	Relative Area	4/2
2	10.00	17.5	
$CH_2(OCH_3)OOH$	12.21	16	54.5/45.5
4	12.05	21	
PROPENYLBENZENE			
2	10.00	42	
3	11.70	43.5	8/92
4	12.05	3.5	

This procedure has been applied to other alkenylbenzenes (5), and the results are summarized in Table II. Reproducibility was generally good, although p-chlorostyrene displayed somewhat less precision than the other olefins.

TABLE II

OZONOLYSIS OF ArCH = CHR

Ar	R	No. of Runs	Mole % 2[a]	Lit. value[b]
p-$H_3COC_6H_4$	H	2	20-21	21±4
p-$H_3CC_6H_4$	H	2	29-30	29±1
p-ClC_6H_4	H	2	61-66	57±1
p-$H_3COC_6H_4$	CH_3	4	68-70	--
p-$H_3CC_6H_4$	CH_3	2	88-89	--
p-ClC_6H_4	CH_3	2	92-93	--
p-HOC_6H_4	CH_3	2	64-65	--

[a] Using the nmr integrator or the DuPont 310 Curve Resolver

[b] Reference 1; data obtained at 25° in 1M methanol in CCl_4

The close accord between these results and those obtained by other techniques (1,2), where such data were available, was indicative of the reasonableness of the assumption that the amounts of 2-4 detectable by nmr actually correspond to those directly generated from primary ozonide heterolysis. An aliquot taken after ozonolysis of p-chloropropenylbenzene was subjected to assay with sodium iodide in refluxing isopropanol (2); its hydroperoxide content was shown to be at least 92% of theoretical.

The tendency of concurrent increase of electron-donating capacity of the para-substituent of the propenylbenzene with mole percent 4, is that which one would predict (1,2). That electron donation by methyl (in intermediate 1) predominates over that due to, e.g. p-anisyl is also not surprising (6). However, the product proportions with the five propenylbenzenes utilized in this study do not give a linear relationship when log (x/1-x) where x = average mole percent 2, is plotted against σ (1). Similar poor fits resulted with other substituent constants: a) σ^+, employed since the postulated aromatic zwitterion (7) contains a positive charge adjacent to the ring; b) (% 2·σ) + (% 4·σ^+), a weighted average of the two parameters based on the observed product ratio. However, as Yukawa and Tsuno (8) have pointed out, a number of examples may be found in the literature where reactions with electron-deficient transition states do not exhibit conventional linear free-energy relationships, the deviation being particularly notable with electron-releasing para-substituents. It is reasonable that decomposition of the polarizable primary ozonide **1** should not show the same proportion of resonance contribution to the substituent constant with variation of the para-substituent in Ar.

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