

GENERATION OF MONOSUBSTITUTED o-BENZYNES FROM
 POLYMERIC REAGENTS VIA HETEROLYTIC FRAGMENTATIONS

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Abstract: Generation of four 4-substituted o-bzynes by heterolytic -- fragmentation reactions is demonstrated.

Arynes have been postulated as intermediates in a variety of processes such as reaction of aryl halides with nucleophiles¹, treatment of o-dihaloaromatic compounds with metals or organolithium reagents², heterolytic fragmentation of o-substituted benzoic acids^{3,4,5}, etc. . However, up to now evidence of such intermediacy has been practically limited to o-bzyne itself, and more incisive experimental work is needed in this field. The Three Phase Test⁶ provides an unambiguous test for reactive intermediates and we have shown how the presence of o-bzyne in fragmentation reactions can be demonstrated by the use of this method⁷. Here we report the application of this technique to demonstrate the generation of 4-substituted o-bzynes, as free species in solution, by --- heterolytic fragmentation reactions.

The polymer-bound precursors were the polymeric diaryliodonium-2-carboxyla-

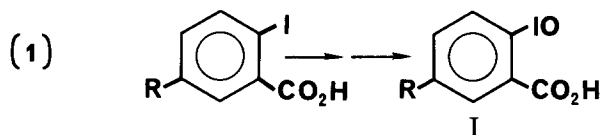
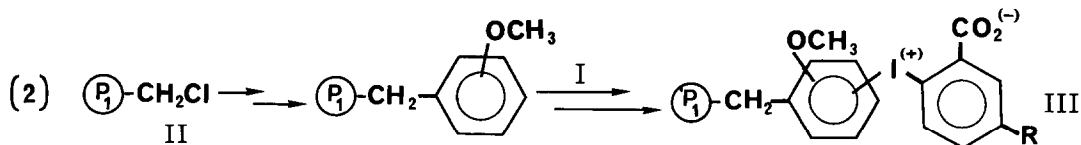


TABLE I

I	R	yield (%)
a	CH ₃	82
b	Cl	70
c	Br	94
d	NO ₂	91



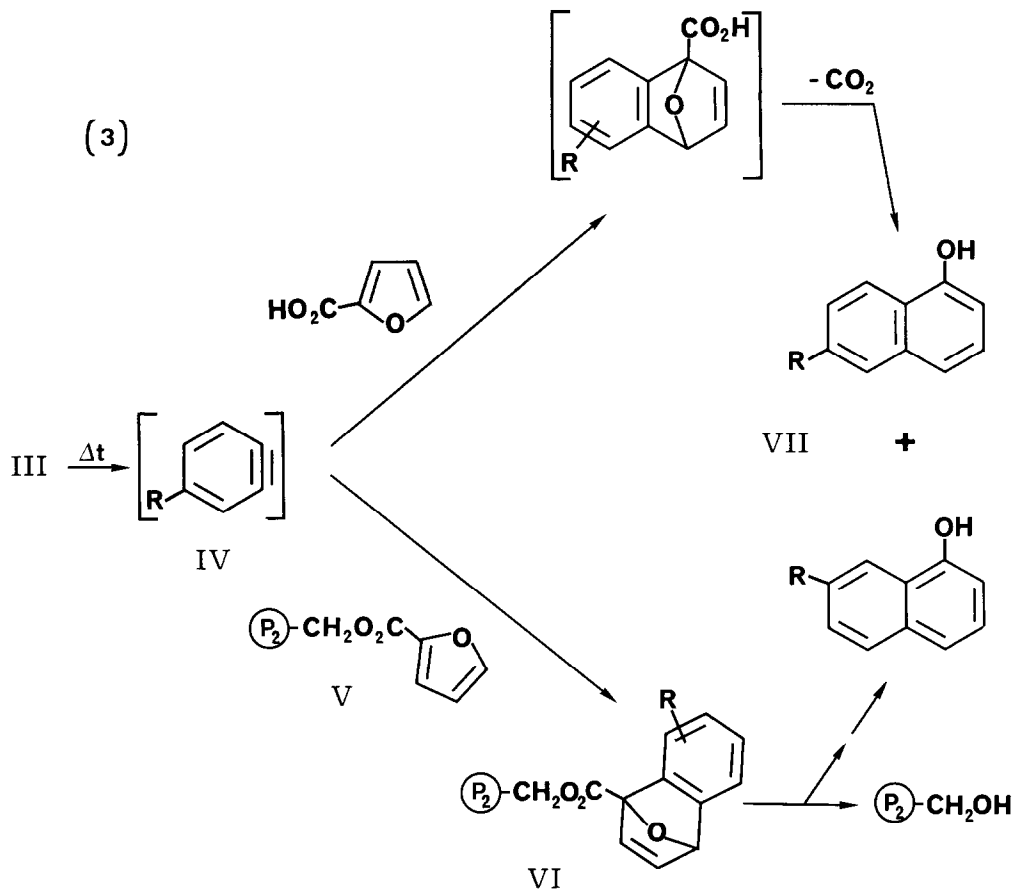
tes III prepared by treatment of macroreticular, 2% crosslinked, chloromethylated polystyrene (3.5 meq Cl/g) with $C_6H_5OCH_3$ and BF_3/Et_2O complex, followed by coupling with an *o*-iodosobenzoic acid (I) in F_3CCOOH/H_2SO_4 , and neutralization with Et_3N (eq. 2)⁸. Functionalization degrees for polymers III, which were -- calculated by weight increase and by thermogravimetric analysis⁷, are given in Table II. Yield, in that table, refers to overall yield from II to III. -- 5-substituted *o*-iodosobenzoic acids I were easily synthesized in excellent -- yields (Table I) by oxidation of the related *o*-iodobenzoic acids with potassium persulfate in sulfuric acid, and then hydrolysis (eq. 1).

TABLE II

III	R	functionalization degree	yield (%)
a	CH ₃	0.52	33
b	Cl	1.07	71
c	Br	0.78	55
d	NO ₂	0.76	61

Thermogravimetric analysis of polymers III showed that decomposition -- always occurs at about 200°C and that the competition between heterolytic -- fragmentation and rearrangement⁷ is affected by the nature of R groups. Thus, when R is a methyl group, behaviour of III is close to the parent compound (R = H) and fragmentation is by far the main process, but when R is an --- electron withdrawing group (III b-d, R = Cl, Br, NO₂) side reaction increases its importance. As an example, the fragmentation/rearrangement ratio decreases from R = CH₃ (IIIa) to R = NO₂ (III d) in a factor of 21.43 .

The thermal decomposition of polymers III (eq. 3) was carried out in a solution of furoic acid in refluxing diethylbenzene, producing in every case an almost equimolecular mixture of 6- and 7-substituted α -naphthols which were identified by spectroscopic analysis and mass spectra as well as by comparison with authentic samples. The intermediacy of 4-methyl, 4-chloro, 4-bromo and 4-nitrobenzyl (IV) as free species in solution was demonstrated by the use of the Three Phase Test. Polymer-bound furoate V⁹ as trapping agent and resins III as precursors were heated and stirred in diethylbenzene at 190°C for 24 h. After saponification of polymeric adducts (VI) followed by acidification, mixtures of 6- and 7-substituted α -naphthols were again obtained.



The Three Phase Test implies that an intermediate is liberated from a -- polymer-bound precursor and pass through the solvent to a second polymer in which it is trapped. This process needs some tenths of a second to be completed¹⁰. Therefore, trapping of these o-arynes in a Three Phase Test shows that lifetimes of free o-arynic intermediates in solution are at least in this range for the experimental conditions outlined above. This represents a lifetime longer than one calculated for gaseous o-benzyne¹¹, but probably not so long as described for a polymer-bound o-benzyne for which the long lifetime is related to pseudodilution or immobilization on the polymeric matrix¹².

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