Homolytic Aromatic Substitution by Phenylethynyl Radicals

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Summary Alkylbenzenes are more reactive than benzene towards phenylethynyl radicals.

THE recently reported[1] decomposition of phenylpropioloyl peroxide and t-butylperoxyphenylpropiolate prompts us to report on a related study. Our interest in homolytic aromatic substitution[2] led us to study the substitution of monosubstituted benzene derivatives by variously hybridized carbon free-radicals.

The decomposition[3] of the cyclohex-1-enoyl peroxide in aromatic solvents affords cyclohex-1-enyl radicals, the substitution pattern of which is similar to that of the phenyl radical.

Phenylpropioloyl peroxide (m.p. 94—95° decomp.), prepared by reaction of phenylpropioloyl chloride and ethereal hydrogen peroxide at $-20°$ in the presence of pyridine, decomposed in benzene and cumene but gave neither diphenylacetylene nor 1-isopropylphenyl-2-phenylacetylene (by g.l.c.) as would be expected from substitution by phenylethynyl radicals (II), if formed, of the aromatic substrates. Further, there were no products resulting from hydrogen abstraction by, or dimerization of, these radicals.† The failure to find any evidence for the production of phenylethynyl radicals supports the results of Simamura and his co-workers, who provided convincing evidence for a new type of induced decomposition for phenylpropioloyl and dicinnamoyl peroxides.[1]

We found that the acetylenic radicals (II) were readily

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† Phenylpropiolic acid was isolated in both cases and bicumyl was found in the reaction in cumene. Similar results were obtained by the decomposition of t-butylperoxyphenylpropiolate.

produced on photolysis of 1-iodo-2-phenylacetylene (I) which, in benzene solution, afforded diphenylacetylene (III; R = H) (75%)[4] and in thiophen gave the two isomeric 1-phenyl-1-thienylacetylenes.

$$\underset{\text{(I)}}{\mathrm{PhC}\vdots\mathrm{C{\cdot}I}} \xrightarrow{h\nu} \underset{\text{(II)}}{\mathrm{PhC}\vdots\mathrm{C}\cdot} + \mathrm{I}\cdot$$

$$\mathrm{PhC}\vdots\mathrm{C}\cdot + \mathrm{RPh} \rightarrow \underset{\text{(III)}}{\mathrm{PhC}\vdots\mathrm{C{\cdot}C_6H_4{-}R}}(o\text{-}, m\text{-}, \text{or } p\text{-})$$

$$\mathrm{R = H, Bu^t, CHMe_2, Et, Me}$$

1-Iodo-2-phenylacetylene (I) was irradiated in an excess of equimolecular mixtures of benzene and t-butylbenzene, cumene ethylbenzene, and toluene in order to determine the isomer distribution ratios and the relative reactivities for the homolytic aromatic phenylethynylation reaction. Analysis by g.l.c. of the reaction mixtures allowed the values of the isomer ratios and of the reactivities relative to benzene ($^{\mathrm{X}}_{\mathrm{H}}K$) to be determined from the relative amounts of the isomeric 1-aryl-2-phenylacetylenes and diphenylacetylene (see Table).

The results show that all the alkylbenzenes investigated are more reactive than benzene. This situation is unlike that found with phenyl,[5] cyclohexyl,[6] and cyclohexenyl[3] radicals. In addition, the percentage of *ortho*-substitution in both t-butylbenzene and cumene is considerably higher than with the other radicals.[3,5,6] Further work is obviously necessary before the character of the phenylethynyl radical is fully understood. However, our results suggest that steric requirements in the substitution step are less than for radicals like phenyl, cyclohexyl, and cyclohexenyl.

Isomer ratios and relative reactivities in homolytic aromatic phenylethynylation[a]

Aromatic derivatives C_6H_5R	1-Aryl-2-phenylacetylene *ortho* %	*meta* %	*para* %	$^{\mathrm{X}}_{\mathrm{H}}K$
t-Butylbenzene	31·7	41·3	27·0	1·60
Cumene	42·2	33·2	24·6	1·70
Ethylbenzene	52·5	25·5	21·0	2·00
Toluene	61·5	38·5		2·25

[a] The determinations were carried out by g.l.c. with a 10% SE 30 or a 10% LAC 728 column. Products were identified by comparison of their i.r. spectra with those of authentic samples, after separation of the components of the reaction mixtures by preparative g.l.c.

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