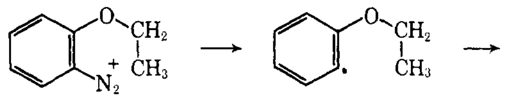
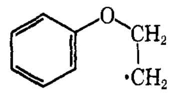
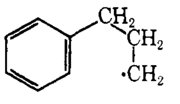
derived from 4-(*o*-aminophenyl)butyric acid gave an intense epr spectrum (see Figure 3) assigned to the radical XIII. The signal was unaffected by addition of ethanol or maleic acid to the reactant solutions.



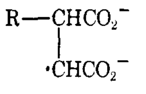
VII VIII



IX



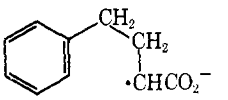
X



$$R\text{—}\underset{\cdot CHCO_2^-}{\underset{|}{C}}HCO_2^-$$

XI, R = o-EtOC$_6$H$_4$

XII, R = o-CH$_3$CH$_2$CH$_2$C$_6$H$_4$



XIII

The radicals IX, X, and XIII are clearly formed by 1,5-hydrogen atom transfer processes (*e.g.*, VIII → IX) proceeding through a six-membered cyclic transition state. In the absence of suitable activating substituents the reaction is relatively slow compared with possible intermolecular processes of aryl radicals, such as hydrogen atom abstraction from ethanol or addition to maleic acid, but it becomes the preferred reaction when the product radical is stabilized by an adjacent carboxylate group.

The foregoing experiments, the conclusions from which have been separately confirmed by analysis of products,[7] clearly establish the utility of epr spectrometry as a technique for investigating the mechanisms of radical reactions in solution.[7a]

Acknowledgment. This work was supported in part by the Australian Research Grants Committee. A. L. J. B. offers thanks for generous hospitality to the Chemistry Department, University of York, where some of the experimental work was conducted.

(7) A. L. J. Beckwith and W. B. Gara, *J. Amer. Chem. Soc.*, **91**, 5691 (1969).

(7a) NOTE ADDED IN PROOF. The use of epr spectrometry to study the cyclization of 5-hexenyl radical has been recently reported by J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969).

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Intramolecular Addition and Hydrogen Atom Transfer Reactions of Aryl Radicals

Sir:

In the preceding communication[1] we described the use of epr spectral techniques to detect the occurrence of intramolecular addition and hydrogen atom transfer reactions in suitably constituted aryl radicals. Further evidence in support of our conclusions is disclosed herein.

When *o*-allyloxybenzenediazonium borofluoride was reduced with Ti^{III} at pH ~8 in a flow system,[2] or with radicals derived from methoxide or isopropoxide ion,[3] the products, identified and estimated by glpc,[4] were allyl phenyl ether (VI), 2,3-dihydro-3-methylbenzo[*b*]furan (IX), and polymeric materials. The yields of VI and IX formed by these methods were small (see Table I), but when *o*-allyloxyiodobenzene (II) was reduced with tributylstannane in benzene[5] a clean reaction occurred and, in most cases, IX was obtained in quantitative yield. Reduction of *o*-(3-butenyl)iodobenzene (III) with tributylstannane was similarly efficient (see Table II) and gave good yields of VII and X. In no case could we detect formation of six-membered cyclic products.

Table I. Reduction of *o*-Allyloxybenzenediazonium Ion and of *o*-Allyloxyiodobenzene

			Yield, %	
Expt	Compd[a]	Reducing agent	IX	VI
1	I	TiCl$_3$[b]	11	2
2	I	MeO$^-$–MeOH[c]	30	<5
3	I	*i*-PrO$^-$–*i*-PrOH[c]	1.5	7
4	II	*n*-Bu$_3$SnH[d]	99	Nil
5	II	*n*-Bu$_3$SnH[e]	99	Trace

[a] Compound I as the borofluoride. [b] 0.008 *M* in water at pH ~8.[1] [c] 2 *M*. [d] 0.172 *M*, in excess. [e] 0.69 *M*, in excess.

Table II. Reduction of *o*-3-Butenyliodobenzene with Tributylstannane[a] in Benzene at 135°

		Yield,[b] %	
[III], *M*	[R$_3$SnH], *M*	VII	X
0.078	0.0	0	0
0.072	0.068	6	56
0.073	0.137	17	80
0.073	0.288	38	62
0.073	0.568	50	50

[a] Initiated with ADIB. [b] Mean results from duplicate experiments.

These results clearly indicate that aryl radicals containing a correctly disposed olefinic function readily cyclize by intramolecular addition. As expected on the basis of epr measurements such cyclization processes evidently proceed very rapidly. Thus, in expt 1, 2, 4, and 5 (see Table I) the high ratio of yields, % IX/% VI, suggests that cyclization of IV is much faster than its reduction by Ti^{III} or its abstraction of hydrogen from methanol or tributylstannane. Only 2-propanol appears to be sufficiently active as a hydrogen atom donor to intercept IV efficiently before it undergoes intramolecular addition.

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(1) A. L. J. Beckwith and W. B. Gara, *J. Amer. Chem. Soc.*, **91**, 5689 (1969).

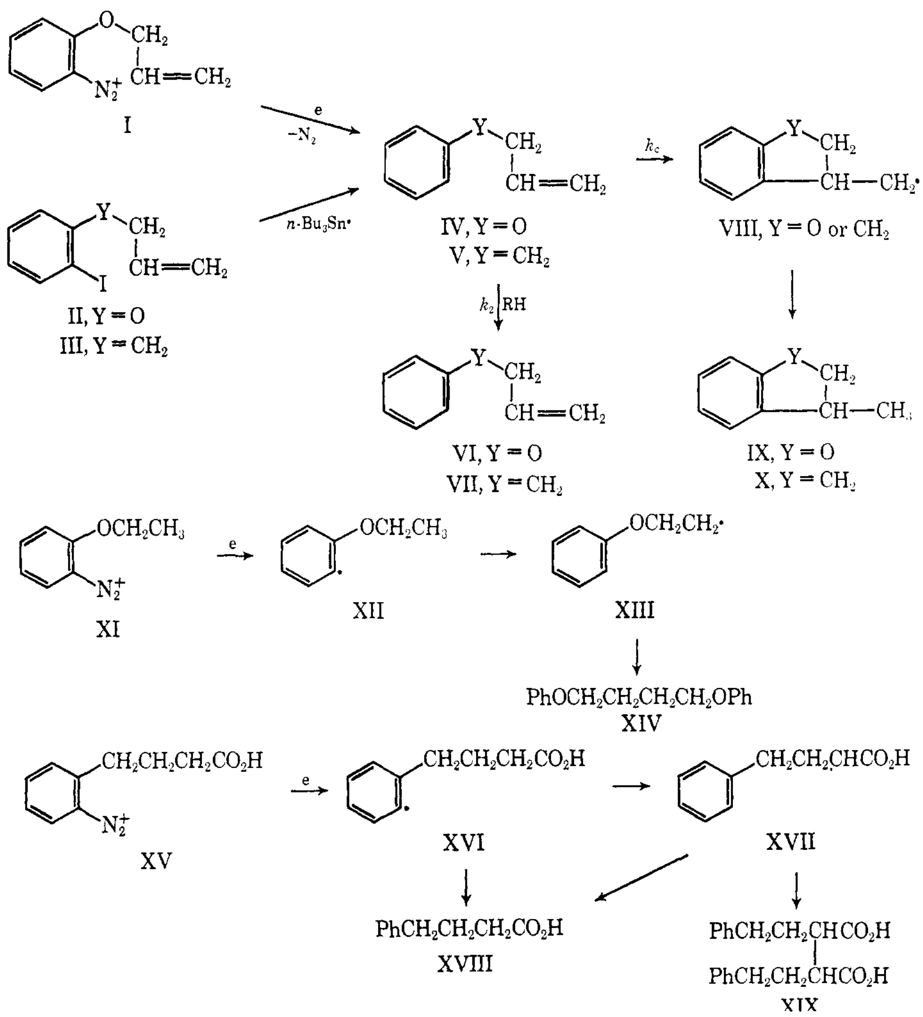
(2) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.*, *B*, 403 (1969).

(3) J. F. Bunnett and H. Takayama, *J. Amer. Chem. Soc.*, **90**, 5173 (1968); *J. Org. Chem.*, **33**, 1924 (1968).

(4) Internal standards were used. Calibration curves were prepared using authentic compounds synthesized by unambiguous routes.

(5) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964), and references cited therein.

Scheme I



Cyclization of *o*-butenylphenyl radical (V) proceeds less rapidly and gives products in yields which may be rationalized in terms consistent with Scheme I. Thus, there is an approximately linear relationship between the ratio of product yields, % VII/% X, and average stannane concentration, from which it may be calculated that $k_c/k_2 \approx 0.5$. On the basis of the reasonable assumption that k_2 will be greater than that for reaction of free methyl with tributylstannane,[6] it may be estimated that k_c is of the order of 10^6 sec^{-1}. For the radical IV k_c is clearly much greater.

Each cyclization reaction proceeded exclusively by 1,5-intramolecular addition; presumably they are controlled by the same stereoelectronic requirements of the transition state which preclude formation of the more thermodynamically stable six-membered product radicals in similar aliphatic systems.[7]

In accord with the results of epr studies we have also succeeded in showing that aryl radicals containing suitable saturated substituents undergo 1,5 hydrogen atom transfer; however the reaction, in the absence of adjacent activating functions, is slow compared with possible intermolecular processes. Thus, reduction of *o*-ethoxybenzenediazonium ion (XI) gave $\sim$2% of 1,4-diphenoxybutane (XIV), the formation of which must be attributed to formation of XIII *via* intramolecular hydrogen atom transfer in XII. The major product was phenetole.

Similar reduction of XV, in which the carboxyl group activates the adjacent position toward hydrogen atom abstraction and stabilizes the product radical (XVII), gave *inter alia* the dimer XIX and phenylbutyric acid (XVIII) in approximate yields of 15 and 30%, respectively. When the starting material (XV) was fully deuterated in the α position 65% of the phenylbutyric acid produced was found by mass spectrometry to contain deuterium attached to the aryl nucleus, thus indicating that the major route for its formation involves the rearranged radical XVII. However, when XVI was generated by Bunnett's method in methanol[3] only 6% of the monomeric product arose *via* rearrangement, indicating that under these conditions intermolecular hydrogen atom transfer from methanol occurs more readily than the intramolecular reaction.

It is noteworthy that these studies confirming the occurrence of intramolecular 1,5 atom transfer and radical addition processes in suitably constituted aryl radicals fulfil predictions based on epr spectral measurements[1] and establish the utility of this technique for probing radical reaction mechanisms.

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(6) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(7) D. L. Struble, A. L. J. Beckwith, and G. E. Gream, *Tetrahedron Lett.*, 3701 (1968), and references cited therein.