dark, is stirred under atmospheric pressure in the presence of air. After quenching with water (30 mL), the solution is extracted with pentane or hexane (3-4 × 10 mL), and the organic phases are washed with brine and dried with $MgSO_4$. The GLC analysis is usually made directly from the pentane or hexane solution of the reaction product(s). After evaporation or distillation of the solvent (by means of a 10-15-cm Vigreux column), the product is purified by column chromatography or distillation.

5-Acetoxy-*exo*-2,3-epoxybicyclo[2.2.1]heptane (exo/endo = 2/8) (10): yield 61%; IR (CCl_4) 1735, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.04 (m, $^1/_2W$ = 18 Hz, 0.8 H C_5-H_{exo}), 4.64 (d, J = 6 Hz, 0.2 H C_5-H_{endo}), 3.29 (dd, J = 19 and 3 Hz) and 3.06 (dd, J = 10 and 3 Hz) ratio 8:2 (2 H, C_2-H and C_3-H_{endo}); 2.76 and 2.58 (2 br s, ratio 8:2, 1 H, C_4-H), 2.49 (br s, 1 H, C_1-H), 1.95-2.15 (m, 1 H), 2.02 and 2.00 (2 s, 3 H, OCCCH_3 endo and exo), 1.26-1.50 (m, part of an AB, J = 10.4 Hz, 1 H, C_7-H anti to epoxide), 1.08 (dt, J = 13 and 3 Hz, 1 H, C_6-H_{endo}), 0.79 (d, J = 10.4 Hz, part of an AB, 1 H, C_7-H syn to epoxide); ^{13}C NMR ($CDCl_3$) **10** endo (≃80%) δ 170.89 (CO), 76.41 (C_5), 50.92 and 48.22 (C_2/C_3), 40.39 (C_4), 36.81 (C_1), 33.0 (C_6), 24.7 (C_7), 20.97 (CH_3); **10** exo (≃20%) δ 170.89 (CO), 73.25 (C_5), 51.69 and 48.08 (C_2/C_3), 42.56 (C_4), 36.45 (C_1), 35.75 (C_6), 23.41 (C_7), 21.15 (CH_3). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.35; H, 7.18.

5-(Acetoxymethyl)-*exo*-2,3-epoxybicyclo[2.2.1]heptane (exo/endo = 3/7) (12): yield 80%; ^1H NMR ($CDCl_3$) δ 3.95-4.12 and 3.77-3.95 (2m, ratio ≃8:2, 2 H, CH_2OAc), 3.15 (dd, J = 12.5 and 3 Hz) and 3.08 (s) ratio ≃8:2 (2 H, C_2-H and C_3-H_{endo}), 2.49 and 2.39 (2br s) ratio ≃8:2 (2 H, C_1-H and C_4-H), 2.17-2.37 (m, 1 H), 2.03 and 2.04 (2s, 3 H, $OCOCH_3$), 0.72-1.9 (3br m and several small m, 4 H (br m are centered at 1.72 ($^1/_2W$ = 27 Hz), at 1.37 (dm, J = 10 Hz), and at 0.79 ($^1/_2W$ = 20 Hz)); ^{13}C NMR ($CDCl_3$) **12** endo (≃70%) δ 170.96 (CO), 65.03 (C_8), 51.06 and 49.07 (C_2/C_3), 39.92 (C_5), 38.19 and 37.16 (C_1/C_4), 28.65 and 27.19 (C_6/C_7), 20.92 (CH_3); **12** exo (≃30%) δ 170.96 (CO), 66.58 (C_8), 51.62 and 51.19 (C_2/C_3), 39.92 (C_5), 36.91 and 37.25 (C_1/C_4), 30.02 (C_6), 23.27 (C_7), 20.92 (CH_3). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.88; H, 7.71.

Preparation of Palladacycle 32. A solution of *cis*-bis(acetonitrile)chloronitrilopalladium(II) (1) (1.34 g, 5 mmol) in 50 mL of acetone was stirred and cooled to 0 °C, and 4 equiv of norbornene (1.88g, 20 mmol) were added rapidly. After a few minutes, a yellow precipitate was formed, and the mixture was stirred until completion of the reaction in the absence of light (≃15 min). The yellow solid was filtered, washed with cold acetone, and dried carefully: yield 1.21 g (86%). The product **32**[17] was used immediately for the different decomposition studies (cf. Table IV).

Oxidation of 32 with $CuCl_2$-LiCl in CH_3CN. A mixture of palladacycle **32** (1.41 g, 5 mmol equiv), $CuCl_2$ (1.34 g, 10 mmol), and LiCl (1.059 g, 25 mmol) (ratio Pd:Cu:Li = 1:2:5) in 50 mL of CH_3CN was stirred at room temperature for 2 days. Water (50 mL) was added and the aqueous solution extracted with ether (4 × 20 mL). The combined organic phases were washed with brine and dried with $MgSO_4$. Removal of the solvent gave a slightly colored liquid (467 mg, 64% with respect to $C_7H_{11}OCl$). The separation, which gave three main products, **34** (57%), **36** (23%), and **37** (6%), could be achieved by preparative column chromatography on silica gel (elution with hexane-CH_2Cl_2 = 95:5).

***exo*-2-Chloro-*syn*-7-hydroxybicyclo[2.2.1]heptane (34)**:[42] IR ($CHCl_3$) 3600, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.08 (s, 1 H, C_7-H_{anti}), 4.07 (partially hidden d of d, 1 H, J = 6.6 and 4.0 Hz, C_2-H_{endo}), 2.74 (s, 1 H, OH), 2.44-2.16 (m, 4 H), 1.8-1.48 (m, 2 H), 1.26-1.02 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 80.39 (C_7), 60.97 (C_2), 48.34 (C_1), 41.75 (C_4), 41.16 (C_3), 25.18 and 24.49 (C_6 + C_5). Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.38; H, 7.68; Cl, 24.05.

***endo*-2-Chloro-*exo*-3-hydroxybicyclo[2.2.1]heptane (37)**:[43] IR ($CHCl_3$) 3600, 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (m, 1 H, $^1/_2W$ = 8.8 Hz, C_2-H_{exo}), 3.66 (t, 1 H, J = 2.2 Hz, C_3-H_{endo}), 2.42 (m, 1 H, $^1/_2W$ = 11 Hz, C_4-H), 2.16 (m, d, 1 H, J = 3.5 Hz, $^1/_2W$ = 8.8 Hz, C_1-H), 1.80-1.16 (2m, 6 H), 1.86 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 83.63 (C_3), 69.87 (C_2), 44.57 (C_4), 42.90 (C_1), 34.52 (C_7), 24.80 (C_5), 21.26 (C_6).

***endo*-2-Chloro-*exo*-3-nitrobicyclo[2.2.1]heptane (36)**: IR ($CHCl_3$) 1550, 1375, 905, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (m, 1 H, $^1/_2W$ = 10 Hz, C_3-H_{endo}), (d, d, 1 H, J = 3.6 and 2 Hz, C_2-H_{exo}), 2.89 (d, m, 1 H, J = 3.6 Hz, C_1-H), 2.62 (m, 1 H, $^1/_2W$ = 9 Hz, C_4-H), 2.05-1.19 (2m, 5 H), 0.86 (m, 1 H, $^1/_2W$ = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 95.47 (C_3), 61.71 (C_2), 44.51 (C_4), 43.40 (C_1), 35.58 (C_7), 26.75 (C_5), 21.16 (C_6). Anal. Calcd for $C_7H_{10}NO_2Cl$: C, 47.88; H, 5.74; N, 7.97; Cl, 20.19. Found: C, 47.89; H, 5.66; N, 7.89; Cl, 20.3.

The other reactions reported in Table IV were carried on **32** in a similar fashion to the one reported above using $CuCl_2$/LiCl in CH_3CN.

Supplementary Material Available: ^{13}C NMR data of cis exo substituted organometallic 2,3-norbornane derivatives **43**, **44**, and **45** and independent preparation of disubstituted norbornene reference compounds **34-37** (1 page). Ordering information is given on any current masthead page.

Iododediazoniation of Arenediazonium Salts Accompanied by Aryl Radical Ring Closure[1]

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Treatment of *o*-(allyloxy)benzenediazonium tetrafluoroborate (**1a**) with sodium iodide in acetone affords the cyclized iodide **2a** in good yield by a mechanism involving the generation and exo cyclization of the aryl radical **6a**. Other diazonium salts (**1b-i**) containing suitable unsaturated side chains behave similarly, but those (**1l**, **1m**) in which there is an *N*-allylsulfonamido group yield mainly products formed by endo cyclization. The diazonium salts **1j** and **1k** do not give cyclized products. Factors affecting the mechanism, rates, and regiochemistry of the reaction are discussed.

Recently, we described experiments involving the use of thiolate ions or copper(II) halides to effect cyclization in the exo mode[2] of aryl radicals derived from *o*-(2-propenyloxy)benzenediazonium tetrafluoroborate (**1a**) or *o*-[(2-methyl-2-propenyl)oxy]benzenediazonium tetrafluoroborate (**1b**).[3] The reactions afforded dihydrobenzofuran derivatives which were functionalized at the

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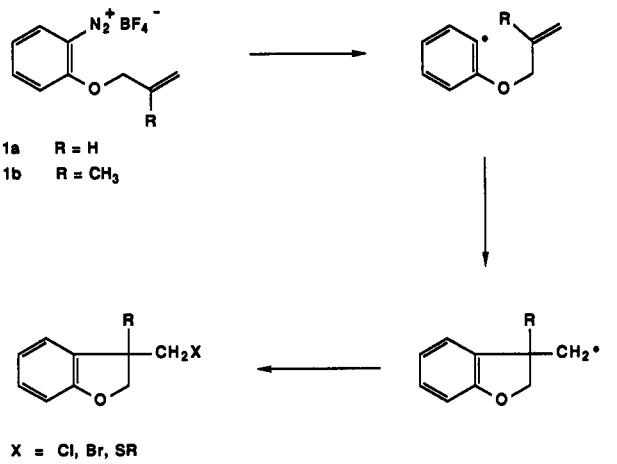
(1) Part of this work has been reported in preliminary form: Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136-137.
(2) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482-483.
(3) Meijs, G. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5890-5893.

0022-3263/87/1952-1922$01.50/0

Scheme I



site of the cyclized radical (Scheme I).

We sought to determine whether similar cyclizations could be achieved when sodium iodide is used as the dediazoniation reagent. We were also interested in investigating the scope and generality of the radical ring closure.

The reaction of arenediazonium salts with sodium iodide in methanol to give aryl iodides has been suggested to follow a free-radical pathway.[4] A homolytic chain mechanism accounts for the inhibition of the reaction by oxygen and the formation of benzene, biphenyl, iodine, and formaldehyde as byproducts in the iodediazoniation of benzenediazonium tetrafluoroborate.[4] Additionally, sodium iodide has been utilized for the generation of aryl radicals which were trapped with carbon disulfide.[5] The Pschorr phenanthrene synthesis has also been carried out by treating appropriate diazonium salts with sodium iodide.[6]

We considered it reasonably likely, therefore, that cyclic products would be obtained from **1a** and **1b** and other diazonium salts containing an appropriate unsaturated ortho substituent provided that the rates of cyclization of the radicals were significantly faster than the direct iodination of the uncyclized aryl radicals.

Results and Discussion

When an acetone solution of *o*-(2-propenyloxy)benzenediazonium tetrafluoroborate (**1a**) was added to a solution of sodium iodide in acetone, the evolution of nitrogen was immediate and the reaction was complete in 10 min. The product, isolated in 86% yield, was the cyclized (iodomethyl)dihydrobenzofuran **2a** (Table I; Chart I). Neither the uncyclized iodoarene **3a** nor the product **4a** of ring closure in the endo mode could be detected. The structure of **2a** was established by mass spectrometry and ^{13}C NMR spectroscopy and was confirmed by reduction with $LiAlH_4$ to the dihydrobenzofuran **5a** (Chart II).

Similarly, when the diazonium salt **1b** was treated with sodium iodide, the cyclized compound **2b** was isolated in 89% yield. Deiodination of **2b** with tributyltin hydride gave the dihydrobenzofuran **5b**.

The high yields of the benzofuran derivatives **2a** and **2b** testify to the efficiency of radical generation and cyclization. The present results are consistent with the radical-chain mechanism deduced from kinetics studies in this laboratory[7] and shown in Scheme II, where ArN_2^+ represents the diazonium ions **1a** or **1b** and R• represents the

Table I. Yields of Dediazoniation Products

diazonium salt	major product	yield, %	minor product	yield, %
1a	**2a**	86		
1b	**2b**	89		
1c	**8**	54[a]	**9**	36[a]
10	**11**	87		
12a	**13a**	84		
1d	**2d**	73		
1e	**14**	73		
1f	**2f**	66	**3f**	12[b]
1g	**2g**	84		
1h	**2h**	>63[c]		
1i	**2i**	65	**3i**	3[b]
1i[d]	**2i**	85	**3i**	5
12b	**13b**	83	**12c**	8
1j	**3j**	60		
1k	**3k**	66		
1l	**4l**	57	**2l**	20
1m	**4m**	50	**2m**	23

[a] Yields determined by ^1H NMR. [b] Yield estimated by GLC. [c] Yield estimated from weight and purity of product (see text and Experimental Section). [d] Reaction conducted with the diazonium hexafluorophosphate.

cyclized radical **7a** or **7b**. Step 1, initiation by reduction of the diazonium ion, rests on the ability of iodide ion to act as a one-electron reductant,[8] while step 5 is also an electron transfer. An important chain propagation step (eq 4) involves iodine atom transfer from I_3^- formed from iodine adventitiously present or generated by combination of iodine atoms.

Scheme II

$$ArN_2^+ + I^- \rightarrow ArN_2^\bullet + I^\bullet \quad (1)$$

$$ArN_2^\bullet \rightarrow Ar^\bullet + N_2 \quad (2)$$

$$Ar^\bullet \rightarrow R^\bullet \quad (3)$$

$$R^\bullet + I_3^- \rightarrow RI + I_2^{\bullet-} \quad (4)$$

$$ArN_2^+ + I_2^{\bullet-} \rightarrow ArN_2^\bullet + I_2 \quad (5)$$

$$I^\bullet + I^\bullet \rightarrow I_2 \quad (6)$$

$$I^- + I_2 \rightarrow I_3^- \quad (7)$$

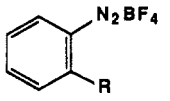
We discount a mechanism for iododediazoniation involving the cage decomposition of an adduct, **3n**, between the terminal nitrogen of the diazonium ion and iodide ion,[9] because the product of cage recombination of the aryl radical and an iodine atom, the open-chain iodide **3a** was not detected in the reaction mixtures.

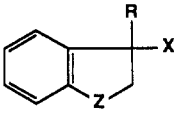
A variety of diazonium salts potentially capable of ring closure was also treated with sodium iodide. The results are summarized in Table I.

Treatment of alkynyl-substituted diazonium salt **1c** with sodium iodide afforded two isomeric iodo olefins **8** and **9** in the ratio 3:2. The olefinic proton in the ^1H NMR spectrum of the major compound, the *Z* isomer **8** was deshielded relative to that in the *E* isomer **9** presumably because of its proximity to the aromatic ring. In the spectrum of the *E* isomer, one of the aromatic protons was shifted considerably downfield on account of its closeness to the iodo group. Although the isomers **8** and **9** were separable by chromatography on silica gel, the major isomer (**8**), decomposed on attempted isolation in a solvent-free state, liberating fumes of iodine; it was, however, moderately stable in solution. The *E* isomer (**9**) did not decompose and could be isolated in pure form.

(4) Singh, P. R.; Kumar, R. *Aust. J. Chem.* **1972**, *25*, 2133–2138.
(5) Benati, L.; Montevicchi, P. C. *J. Org. Chem.* **1976**, *41*, 2639–2640.
(6) Chauncy, B.; Gellert, E. *Aust. J. Chem.* **1969**, *22*, 993–995.
(7) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Org. Chem.*, in press.
(8) Waters, W. A. *J. Chem. Soc.* **1937**, 113–117.
(9) Hantzsch, A. *Chem. Ber.* **1895**, *28*, 676–687.

Chart I





1a R = $OCH_2CH{=}CH_2$

1b R = $OCH_2(CH_3)C{=}CH_2$

1c R = $OCH_2C{\equiv}CH$

1d R = $OCH_2CH{=}CHCH_3$ (trans)

1e R = OCH_2 

1f R = $CH_2CH_2CH{=}CH_2$

1g R = $N(COCH_3)CH_2CH{=}CH_2$

1h R = $N(COCH_3)CH_2(CH_3)C{=}CH_2$

1i R = $OCH_2CH_2CH{=}CH_2$

1j R = $OCH_2CH_2CH_2CH{=}CH_2$

1k R = $CO_2CH_2CH{=}CH_2$

1l R = $SO_2N(CH_2CH{=}CH_2)_2$

1m R = $SO_2NHCH_2CH{=}CH_2$

2a Z = O; X = CH_2I; R = H

2b Z = O; X = CH_2I; R = CH_3

2d Z = O; X = $CHICH_3$; R = H

2f Z = CH_2; X = CH_2I; R = H

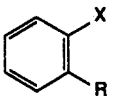
2g Z = $N(COCH_3)$; X = CH_2I; R = H

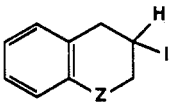
2h Z = $N(COCH_3)$; X = CH_2I; R = CH_3

2i Z = OCH_2; X = CH_2I; R = H

2l Z = $SO_2N(CH_2CH{=}CH_2)$; X = CH_2I; R = H

2m Z = SO_2NH; X = CH_2I; R = H





4a Z = O

4l Z = $SO_2N(CH_2CH{=}CH_2)$

4m Z = SO_2NH

3a R = $OCH_2CH{=}CH_2$; X = I

3f R = $CH_2CH_2CH{=}CH_2$; X = I

3i R = $OCH_2CH_2CH{=}CH_2$; X = I

3j R = $OCH_2CH_2CH_2CH{=}CH_2$; X = I

3k R = $CO_2CH_2CH{=}CH_2$; X = I

3n R = $OCH_2CH{=}CH_2$; X = N_2I

The expected cyclized iodide **11** (Chart III) was isolated in 87% yield when the chloro-substituted diazonium salt **10** was treated with sodium iodide. Similarly, the nitro-substituted diazonium salt **12a** afforded the benzofuran derivative **13a** in good yield.

When *o*-(*trans*-2-butenyloxy)benzenediazonium tetrafluoroborate (**1d**) was stirred with sodium iodide solution, two diastereoisomeric cyclized iodo compounds, **2d**, were obtained in the ratio 64:36. These isomers were separated by chromatography on silica gel. Both of the compounds, on reduction with $LiAlH_4$, afforded 3-ethyl-2,3-dihydrobenzofuran (**5d**), but we were unable to decide which diastereoisomer was which on the basis of spectral data.

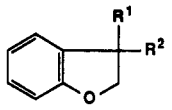
A spirocyclic iodide, **14**, was isolated in 73% yield, after the diazonium salt **1e** had been treated with sodium iodide. Reduction of **14** with $LiAlH_4$ gave the spiroalkane **15** in 71% yield. Both chromatographic and ^{13}C NMR examination suggested that the spiro iodide was isomerically pure. The stereochemistry was assigned by means of ^{13}C NMR spectroscopy. The quaternary aromatic carbon that was not attached to the heteroatom resonated at δ 130.6 in the spiro iodide. In the reduced compound **15**, however, the corresponding carbon resonated at δ 135.6. The 5 ppm upfield shift in **14** relative to **15** is consistent with steric compression.[10] The spectral positions of the other aromatic carbons were relatively unaffected by the removal of the iodo group. This stereochemical assignment places the iodo group in the position which appears to be favored on steric grounds. In the alternative stereoisomer, a more severe steric interaction is expected to exist between the benzofuran C-2 hydrogens and the iodo group.

The indane derivative **2f** was isolated in 66% yield when the diazonium salt **1f** was treated with sodium iodide solution. This product, however, was accompanied by a small quantity of the uncyclized iodide **3f**. It is noteworthy that the rate of cyclization of the aryl radical **6f** appears to be sufficiently slow to allow its interception by the iodinating species before cyclization. Recent data indicate that the rate constant for cyclization of the aryl radical **6f** is considerably less than that for the radical **6a** at 20 °C.[11]

(10) Wihrli, F. W.; Wirthlin, T. *Interpretation of ^{13}C NMR Spectra*; Heyden: London, 1976.

(11) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464–465. Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 795–802.

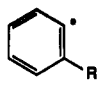
Chart II



5a $R^1 = H$; $R^2 = CH_3$

5b $R^1 = CH_3$; $R^2 = CH_3$

5d $R^1 = H$; $R^2 = CH_2CH_3$



6a $R = OCH_2CH{=}CH_2$

6f $R = CH_2CH_2CH{=}CH_2$

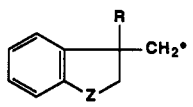
6g $R = N(COCH_3)CH_2CH{=}CH_2$

6i $R = OCH_2CH_2CH{=}CH_2$

6j $R = OCH_2CH_2CH_2CH{=}CH_2$

6k $R = CO_2CH_2CH{=}CH_2$

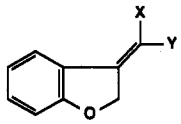
6m $R = SO_2NHCH_2CH{=}CH_2$



7a Z = O; R = H

7b Z = O; R = CH_3

7l Z = $SO_2N(CH_2CH{=}CH_2)$; R = H



8 X = H; Y = I

9 X = I; Y = H

The synthesis of indoline derivatives by radical cyclization was also investigated. The diazonium salt **1g**, after treatment with sodium iodide solution, afforded the cyclized indoline **2g** in good yield. The rate constant for cyclization of the radical **6g** has not been reported, but this radical evidently cyclizes faster than **6f**, since uncyclized products were not obtained. The expected indoline derivative **2h** was obtained in moderate yield when the diazonium salt **1h** was treated with sodium iodide. The crude reaction mixture, however, contained a number of other, unidentified compounds, and the purification of **2h** was difficult.

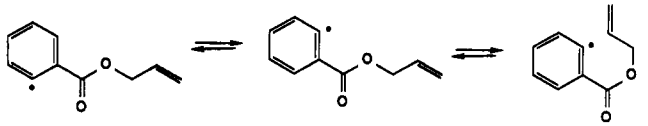
In order to survey further the scope of the sodium iodide ring closure, we examined the reactions of a number of other diazonium salts suitably constituted for cyclization.

When the diazonium tetrafluoroborate **1i**, which was obtained as an oil, was treated with sodium iodide, the cyclized iodide, the chroman derivative **2i** was obtained in moderate yield. The uncyclized iodide **3i** was also formed in small yield. However, when the corresponding hexafluorophosphate salt, which was crystalline and more stable, was treated with sodium iodide, the yield of **2i** was increased to 85%. A small amount of the uncyclized product **3i** was also detected. The formation of **3i** was expected, since the rate of cyclization of the radical **6i**, like that of **6f**, the reaction of which also gave some uncyclized material, is much less than that of **6a**.[11] The nitro-substituted diazonium salt **12b** gave the chroman derivative **13b** as the major product; a small amount of uncyclized iododediazoniation product was also obtained.

All attempts to effect the cyclization of *o*-(4-pentenyloxy)benzenediazonium tetrafluoroborate (**1j**) with sodium iodide failed and the reactions afforded only the uncyclized iodo compound **3j**. Even when the reaction mixture was made ten times more dilute than normal in an attempt to retard the bimolecular iodination of the aryl radical before cyclization, the only product obtained was the uncyclized iodide **3j**. Evidently, the cyclization of the radical **6j** is significantly slower than the trapping of the uncyclized radical with the iodinating reagent.

This observation as well as the previous one that small amounts of the uncyclized iodide **3i** were obtained from the diazonium salt **1i** implies that the ring closure induced by sodium iodide is limited to the synthesis of five- and six-membered rings by cyclization in the exo mode. The formation of six-membered rings is just sufficiently fast to compete with intermolecular trapping of the uncyclized radical by a triiodide ion. The formation of seven-membered rings, however, is too slow. It is reasonable to assume that the formation of larger rings would be even less favorable. The possibility should also be noted that the ring closure of the radical **6i** may be faster than many other exo mode 1,6-ring closures, and that the slowness of such ring closures may lead to rather more uncyclized material being obtained. Although the experimental data for a variety of 1,6-exo mode ring closures are not yet available, it is not unreasonable to suggest analogy to 1,5-ring closures, where oxygen in the 3-position relative to the radical center strongly enhances the rate of ring closure.[11-14]

Treatment of *o*-(2-propenyloxy)carbonylbenzenediazonium tetrafluoroborate (**1k**) with sodium iodide afforded the uncyclized iodo compound **3k**; no ring-closed products were detected. Apparently, the cyclization of **6k** is too slow to compete with direct iodination. We suggest that this reflects the interplay of several factors. First, cyclization to form six-membered rings in the exo mode is slower than similar cyclizations which form five-membered rings.[11-13,15] For example, *o*-(3-butenyloxy)phenyl radical cyclizes some 60 times slower than does *o*-(2-propenyloxy)phenyl radical (**6a**);[11] 6-heptenyl radical cyclizes more than 30 times slower than does 5-hexenyl.[15] Second, molecular geometry is altered by the introduction of the carbonyl group. However, the most important factor is probably the preferential adoption of conformations unsuitable for ring closure. Thus of the possible conformers generated by rotation about the CO–O bond those (e.g., **16**, **17**) in which the aryl and allyl groups are anti are likely to be the more stable. Furthermore of the two conformers **16** and **17**, which allow maximum conjugation between the carbonyl and aryl moieties, that which reflects the conformation of the parent diazonium salt will be initially formed. Since electrostatic interaction between the carbonyl oxygen and the diazonium group is likely to favor a **16**-like conformation, we conclude that the radical **6k** is probably generated initially as the conformer **16**. Consequently, if interconversion of the conformations **16**–**18** is slow[16] relative to iodination, then uncyclized material will result.[16]



16 17 18

The diazonium salt **1l** on treatment with sodium iodide, afforded two cyclic compounds. The compound **2l** formed

(12) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100; Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 162.

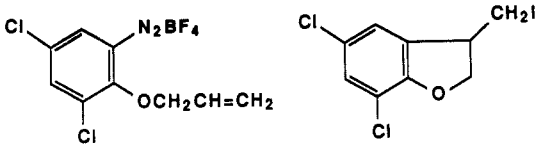
(13) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925–3941.

(14) Smith, T. W.; Butler, G. B. *J. Org. Chem.* **1978**, *43*, 6–13.

(15) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472–473.

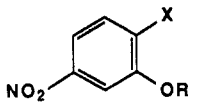
(16) For evidence of the effect of restricted rotation about an aryl–carbonyl bond on a radical reaction, see: Cohen, T.; Smith, K. W.; Swerdloff, M. W. *J. Am. Chem. Soc.* **1971**, *93*, 4303–4304.

Chart III



10

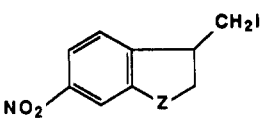
11



12a X = N_2BF_4; R = $OCH_2CH{=}CH_2$

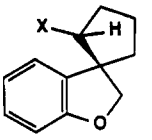
12b X = N_2BF_4; R = $OCH_2CH_2CH{=}CH_2$

12c X = I; R = $OCH_2CH_2CH{=}CH_2$



13a Z = O

13b Z = OCH_2

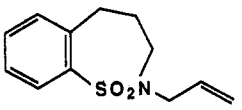


14 X = I

15 X = H

in the smaller yield was that expected from a single cyclization in the exo mode. The structure was assigned by using ^{13}C NMR spectroscopy. The major compound, however, was the iodide **4l**, formed by ring closure in the endo mode. The structure of this compound was also assigned on the basis of its ^{13}C NMR spectrum and was confirmed by reduction with tributyltin hydride; the reduced product did not have a high-field doublet in its ^1H NMR spectrum. Instead, a complex multiplet between δ 1.5 and 2.0, consistent with two methylenes split by two further sets of methylenes, was present.

Although, in principle, a second cyclization of the radical **7l** is possible, products were not found from this pathway. It is anticipated that the second cyclization, which is formally that of an aliphatic "6-heptenyl" system, would be slow relative to the aryl radical cyclizations.[12] Accordingly, it is not surprising that the radical **7l** is trapped before further cyclization. Similarly, the geometry of the radical **19** would not be conducive to further cyclization.



19

Treatment of **1m** with sodium iodide solution gave a similar result. The major product was the iodide **4m**, derived from cyclization in the endo mode, but some exo product **2m** was also formed. The products were unambiguously identified by ^{13}C NMR spectroscopy.

It is not clear why the radicals derived from the diazonium salts **1l** and **1m** should cyclize preferentially in the endo mode. If the reasonable assumption that the cyclization step is irreversible is accepted, then the most likely explanation is that the sulfonamido group changes the dimensions of the aryl radicals derived from **1l** and **1m** in such a way as to reduce the strain energy of the endo transition structure and increase that of the exo. Unfortunately, the lack of appropriate parameters precludes the application of molecular mechanics calculations.[13] However, it is noteworthy that in acyclic systems relatively small structural changes have profound effects on transition structure strain energies.[13] Another possibility is that the preferred endo cyclization reflects the enhanced electrophilicity of the aryl radical due to the presence of the electron-withdrawing sulfonamido substituent. However, the fact that the electrophilic radicals derived from **12a** and **12b** undergo exclusive exo ring closure weakens this hypothesis. We are therefore searching for further examples of aryl radical cyclization in the endo mode in order to provide insight into this unexpected regiochemistry.

Conclusion. The results show that the reaction between sodium iodide and suitably constituted arenediazonium salts affords cyclized products in good yield provided that the cyclization of the aryl radical is sufficiently fast compared with its direct iodination. The reaction may be used for the formation of five- or six-membered rings, and since the products contain a good nucleofuge in the iodo group and are thus very suitable for further elaboration, the method has considerable synthetic potential.

Experimental Section

Materials and Methods. Acetone (May and Baker, AR Grade) was redistilled and deoxygenated for several minutes with a slow stream of nitrogen before use. *o*-(Propenyloxy)benzenediazonium tetrafluoroborate (**1a**),[17] *o*-[(2-methyl-2-propenyl)oxy]benzenediazonium tetrafluoroborate (**1b**),[17] *o*-(3-butenyloxy)benzenediazonium tetrafluoroborate (**1i**),[17] 2,4-dichloro-6-nitrophenol,[18] 2-propenyl *o*-nitrobenzoate,[19] 2-(2-propenyloxy)-4-nitroaniline,[20] 2-acetamido-5-nitrophenol,[21] 1-(bromomethyl)-cyclopentene,[22] *o*-nitro-*N*-2-propenylaniline,[23] and *o*-(2-propenyloxy)iodobenzene[13] were prepared by the literature methods. Instrumentation has been described previously.[3]

The GLC columns used were as follows: column A, 3.0 m × 3.2 mm, 10% Apiezon M on Varaport 30 (80–100 mesh); column B, 1.5 m × 3.2 mm, 15% SE-30 on Varaport 30 (80–100 mesh); column C, 1.5 m × 3.2 mm, 1% SE-30 on Varaport 30 (100–200 mesh); column D, 3.0 m × 3.2 mm, 5% Carbowax 20 M on Varaport 30 (100–200 mesh).

***o*-(2-Propynyloxy)aniline.** Alkylation[24] of *o*-acetamidophenol with 3-bromopropyne gave *o*-(2-propynyloxy)acetanilide which was hydrolyzed[24] to give the require amine (85%) as an oil: bp 110–112 °C (1.5 mm).

***o*-(4-Pentenyloxy)acetanilide.** Alkylation[24] of acetamidophenol with 5-bromopentene gave the required amide (80%) as an oil which was >95% pure as shown by the ^1H NMR spectrum.

(17) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593–600.
(18) Brown, J. P.; McCall, E. B. *J. Chem. Soc.* **1955**, 3681–3687.
(19) Jacquemain, R.; Moskovits, A. *C. R. Hebd. Seances Acad. Sci.* **1937**, *204*, 134–136.
(20) Verkade, P. E.; Roelfzemn, H.; Meerburg, W.; Bosma, G. S. K. *Recl. Trav. Chim. Pays-Bas* **1947**, *66*, 374–382.
(21) Newberry, G.; Phillips, M. A. *J. Chem. Soc.* **1928**, 116–126.
(22) Pal, P. R.; Skinner, C. G.; Dennis, R. L.; Shive, W. *J. Am. Chem. Soc.* **1956**, *78*, 5116–5118.
(23) Ashton, B. W.; Suschitzky, H. *J. Chem. Soc.* **1957**, 4559–4562.
(24) Tiffany, B. D. *J. Am. Chem. Soc.* **1948**, *70*, 592–594.

A small portion of the oil, on trituration with light petroleum, gave crystals: mp 32–33 °C; MS, m/z 219 (55%, M^+), 109 (100%); ^1H NMR δ 1.5–2.5 (m, 7 H), 3.91 (t, J = 6 Hz, 2 H), 4.7–5.2 (m, 2 H), 5.4–6.1 (m, 1 H), 6.4–7.0 (m, 3 H), 7.7 (br s, 1 H), 8.0–8.4 (m, 1 H); IR 3330, 1680 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 71.52; H, 7.72.

o-(4-Pentenyloxy)aniline. o-(4-Pentenyloxy)acetanilide was refluxed with 20% aqueous potassium hydroxide for 12 h to give the corresponding amine (84%) as an oil: bp 83–85 °C (0.3 mm); MS, m/z 177 (36%, M^+), 109 (100%); ^1H NMR δ 1.5–2.5 (m, 4 H), 3.60 (s, 2 H), 3.93 (t, J = 6.5 Hz, 2 H) 4.8–5.2 (m, 2 H), 5.4–6.1 (m, 1 H), 6.5–7.1 (m, 4 H); IR 3465, 3380, 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 74.44; H, 8.43.

3,5-Dichloro-2-(2-propenyloxy)nitrobenzene. An efficiently stirred mixture of 2,4-dichloro-6-nitrophenol (39 g), anhydrous potassium carbonate (29 g), 3-bromopropene (25 g), and acetone (50 mL) was heated at reflux until the red color of the phenoxide anion had disappeared (3 days). The reaction mixture was then diluted with water and the product was isolated by extraction with $CHCl_3$. After several recrystallizations (EtOH/water) the pure ether (31 g, 67%) was obtained: mp 37.5–38 °C; MS, m/z 251, 249, 247, 195, 193, 191; ^1H NMR δ 4.70 (d, J = 6 Hz, 2 H), 5.2–5.7 (m, 2 H), 5.8–6.7 (m, 1 H), 7.6–7.9 (m, 2 H); IR (Nujol) 3075, 1540, 1350 cm^{-1}. Anal. Calcd for $C_9H_7Cl_2NO_3$: C, 43.58; H, 2.84; N, 5.65. Found: C, 43.60; H, 2.69; N, 5.41.

3,5-Dichloro-2-(2-propenyloxy)aniline. Stannous chloride reduction[25] (8 h) of 3,5-dichloro-2-(2-propenyloxy)nitrobenzene followed by basic (NH_4OH) workup afforded the required amine (56%) as an oil, which was shown by GLC (column C, 150 °C) to contain <10% of the starting material. This oil was used without further purification for the preparation of the diazonium salt. A small portion of the amine was purified by flash chromatography (10% CH_2Cl_2/light petroleum): $n^{22.5}D$ 1.5758; MS, m/z 221, 219, 217, 180, 178, 176; ^1H NMR δ 4.03 (s, 2 H), 4.50 ("d", J = 6 Hz, 2 H), 5.1–5.7 (m, 2 H), 5.8–6.6 (m, 1 H), 6.6–6.9 (m, 2 H); IR 3480, 3390 cm^{-1}. Anal. Calcd for $C_9H_9Cl_2ON$: C, 49.57; H, 4.16; m/z 217.0061. Found: C, 49.78; H, 4.39; m/z 217.0064.

o-(*trans*-2-Butenyloxy)aniline. A solution of o-(*trans*-2-butenyloxy)nitrobenzene[26] (10 g) in ether (250 mL) was stirred with aluminium amalgam[26] (7.0 g) in a 1-L flask fitted with an efficient reflux condenser while water (to a total volume of 6.0 mL) was added in small portions. When boiling had ceased and the reduction was shown by GLC (column C, 150 °C) to be complete, the mixture was filtered through Celite. The solvent was removed from the dried filtrate, and the residue was distilled to afford the required amine (4.9 g, 58%): bp 91–92 °C (0.4 mm); MS, m/z 163 (24%, M^+), 109 (100%); ^1H NMR δ 1.6–1.8 (m, 3 H), 3.68 (s, 2 H), 4.2–4.6 (m, 2 H), 5.5–5.9 (m, 2 H), 6.4–6.8 (m, 4 H); ^{13}C NMR δ 17.7, 69.1, 112.2, 115.3, 118.4, 121.3, 126.7, 130.0, 136.8, 146.6; IR 3400, 3310, 1670 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.60; H, 8.02. Although this compound appeared homogeneous by GLC (column B, 150 °C) and TLC, small peaks appeared in the ^{13}C NMR spectrum at δ 13.4, 64.4, 126.2, and 128.2, which were of intensity <20% of the main peaks. They were tentatively assigned to the cis isomer.

o-Nitro-*N*-2-propenylbenzenesulfonamide. Allylamine (8.6 g) was added dropwise to a stirred mixture of potassium carbonate (21 g), o-nitrobenzenesulfonyl chloride (33 g), and CH_2Cl_2 (185 mL). When the addition was complete, the mixture was further stirred for 2 h, and then water (40 mL) and 10% aqueous hydrochloric acid were successively added dropwise. The organic layer was then separated and washed with 10% aqueous hydrochloric acid, saturated sodium bicarbonate solution and water. The solvent was removed under reduced pressure to afford the required amide (28 g, 78%): mp 74–75 °C (from toluene/light petroleum); MS, m/z 186 (69%, $M^+ - C_3H_6N$), 56 (100%); ^1H NMR δ 3.78 (dd, J = 5.5, 5 Hz, 2 H), 5.0–6.2 (m, 4 H), 7.6–8.0 (m, 3 H), 8.0–8.4 (m, 1 H): IR (Nujol) 3335, 1545, 1370, 1340, 1180 cm^{-1}. Anal. Calcd for $C_9H_{10}N_2SO_4$: C, 44.62; H, 4.16; N, 11.56. Found: C, 44.64; H, 4.31; N, 11.50.

o-Amino-*N*-2-propenylbenzenesulfonamide. Degreased iron powder (40 g) was mixed with concentrated HCl (7 mL) and then was dried under vacuum. A stirred mixture of the foregoing nitro compound (20 g), benzene (40 mL), and the iron powder (40 g) was boiled under reflux for 3 h, during which time small portions of water (to a total volume of 3.0 mL) were added periodically. The mixture was filtered, and the solid was washed with small portions of hot benzene until the washings were clear. The combined benzene phases were washed with water and extracted three times with 10% aqueous hydrochloric acid. After the combined acid extracts had been washed with benzene, they were made basic with 10% aqueous sodium hydroxide and extracted twice with ether. The combined ether extracts were washed with water and dried and the solvent was removed to afford the amine (14 g, 80%) as a yellow oil: bp 148–156 °C (0.2 mm); $n^{21}D$ 1.5823; MS, m/z 212 (13%, M^+), 83 (90%), 56 (100%); ^1H NMR δ 3.52 (dd, J = 5.5, 5.5 Hz, 2 H), 4.5–5.4 (m, 5 H), 5.4–6.1 (m, 1 H), 6.6–7.0 (m, 2 H), 7.2–7.6 (m, 1 H), 7.6–7.8 (m, 1 H); IR 3475, 3385, 3300, 1620, 1320, 1160 cm^{-1}. Anal. Calcd for $C_9H_{12}N_2SO_2$: C, 50.93; H, 5.70; N, 13.20. Found: C, 50.85; H, 5.82; N, 13.28.

o-Nitro-*N*,*N*-di-2-propenylbenzenesulfonamide. The reaction between diallylmine and o-nitrobenzenesulfonyl chloride as described above, afforded the required nitroamide (79%): bp 200 °C [block] (0.12 mm); mp 29–30 °C; MS, m/z 283 (1%, $M^+ + 1$), 186 (100%); ^1H NMR δ 3.85 (d, J = 6 Hz, 4 H), 4.9–5.3 (m, 4 H), 5.3–6.0 (m, 2 H), 7.4–8.1 (m, 4 H): IR 1545, 1370, 1355, 1161 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_4S$: C, 51.07; H, 5.00; N, 9.92. Found: C, 51.19; H, 5.06; N, 10.09.

o-Amino-*N*,*N*-di-2-propenylbenzenesulfonamide. Treatment of the foregoing nitro compound with iron powder and water gave the amine (79%): mp 43.5–44.5 °C (from toluene/hexane); MS, m/z 252 (6%, M^+), 96 (100%); ^1H NMR δ 3.75 (d, J = 6 Hz, 4 H), 4.8–5.3 (m, 6 H), 5.4–6.1 (m, 2 H), 6.6–7.6 (m, 4 H); IR 3240, 3325, 1322, 1142 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2O_2S$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.11; H, 6.21; N, 11.26.

2-Propenyl o-Aminobenzoate. 2-Propenyl o-nitrobenzoate[19] was reduced in benzene solution with iron powder and water to afford the required amine (76%): bp 104–105 °C (0.4 mm); MS m/z 177 (48%, M^+), 65 (100%); ^1H NMR δ 4.75 (d, J = 5 Hz, 2 H) 5.0–6.5 (m, 5 H), 6.5–6.8 (m, 2 H), 7.0–7.4 (m, 1 H), 7.7–8.1 (m, 1 H); IR 3430, 3330, 1650 cm^{-1}. Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.42; H, 6.49.

2-(3-Butenyloxy)-4-nitroacetanilide. 5-Nitro-2-acetamidophenol was alkylated[24] with 4-bromobutene to give the required ether (38%): mp 90–91 °C; MS, m/z 250 (21%, M^+), 55 (100%); ^1H NMR δ 2.22 (s, 3 H), 2.61 ("q", J = 6 Hz, 2 H), 4.15 (t, J = 6 Hz, 2 H), 4.9–5.4 (m, 2 H), 5.5–6.3 (m, 1 H), 7.5–7.9 (m, 2 H), 8.00 (br s, 1 H), 8.42 (d, J = 9 Hz, 1 H); ^{13}C NMR δ 24.9 (q), 33.4 (t), 68.5 (t), 106.5 (d), 117.8 (d), 118.1 (t), 118.4 (d), 134.2 (d), 134.5 (t), 143.2 (s), 145.6 (s), 168.8 (s); IR (Nujol) 3320, 1675, 1500, 1345 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64. Found: C, 57.83; H, 5.74.

2-(3-Butenyloxy)-4-nitroaniline. The foregoing amide was hydrolyzed[24] to give the required amine (74%): mp 49–50 °C (from EtOH, low temperature); MS, m/z 208 (73%, M^+), 154 (94%), 55 (100%); ^1H NMR δ 2.53 ("q", J = 6.5 Hz, 2 H), 4.05 (t, J = 6.5 Hz, 2 H), 4.63 (br s, 2 H), 4.8–5.4 (m, 2 H), 5.5–6.2 (m, 1 H), 6.55 (d, J = 8.5 Hz, 1 H), 7.4–7.9 (m, 2 H); IR (Nujol) 3490, 3390, 1620, 1520, 1320 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.69; H, 5.81. Found: C, 57.93; H, 5.83.

o-(1-Cyclopentenylmethoxy)nitrobenzene. 1-(Bromomethyl)cyclopentene (3.0 g) was added to a stirred suspension of o-nitrophenol (2.6 g) in acetone (6.0 mL) and anhydrous potassium carbonate (2.9 g), and the mixture was boiled under reflux overnight. The mixture was then diluted with water and extracted twice with ether. The combined ether extracts were thoroughly washed with 10% aqueous sodium hydroxide solution and water, and the solvent was removed to afford the required ether (3.6 g, 88%): mp 32–32.5 °C (from CH_2Cl_2/light petroleum, low temperature); MS (15 eV), m/z 219 (1%, M^+), 81 (94%), 80 (100%); ^1H NMR δ 1.5–2.7 (m, 6 H), 4.65 (s, 2 H), 5.72 (s, 1 H), 6.7–7.9 (m, 4 H); IR (Nujol) 1535, 1350 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98. Found: C, 65.68; H, 5.81.

o-(1-Cyclopentenylmethoxy)aniline. The foregoing nitro compound was reduced with aluminum amalgam as described for

(25) Hodgson, H. H.; Smith, E. W. *J. Chem. Soc.* **1935**, 671–674.
(26) Martynova, V. P.; Bunina-Kirvorukova, L. I.; Bal'yan, Kh. V. *Zh. Org. Khim.* **1970**, *6*, 2099–2104.
(27) Wislicenus, H.; Kaufmann, L. *Chem. Ber.* **1895**, *28*, 1323–1327.

the preparation of *o*-(*trans*-2-butenyloxy)aniline to afford the required amine (86%) as an oil: bp 102–106 °C (0.15 mm); $n^{14.5}_D$ 1.5767; MS, *m/z* 189 (59%, M^+), 109 (100%); ^1H NMR (CCl_4) δ 1.6–2.7 (m, 6 H), 3.50 (s, 2 H), 4.47 (s, 2 H), 5.60 (s, 1 H), 6.2–6.8 (m, 4 H); IR 3450, 3370 cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99. Found: C, 76.12; H, 7.77.

***o*-(3-Butenyl)aniline.** A solution of 4-bromobutene (13.5 g) in dry THF (75 mL) was added dropwise under nitrogen to magnesium turnings (2.7 g), activated with a crystal of iodine, in boiling dry THF (50 mL). After the addition was complete, the mixture was boiled under reflux for an additional 4 h. The cooled Grignard reagent was added dropwise under nitrogen to a stirred solution of nitrobenzene (6.1 g) in dry THF (125 mL) at −40 °C. After 15 min of stirring, the mixture was cooled to −78 °C, and a mixture of concentrated hydrochloric acid and THF was then added over 3 min. The combined extracts, obtained by dilution of this reaction mixture with water and repeated extraction with ether, were washed three times with water and dried. Removal of the solvent under reduced pressure afforded a dark brown oil (7 g), which was treated overnight in the usual way with aluminum amalgam (7 g) and water (5 mL). The product from this reduction was distilled from zinc dust (500 mg) and the fraction with bp 60–90 °C (0.7 mm) (1.5 g) was collected. Since this red/brown oil was suspected still to contain hydroxylamines and azo compounds, it was treated in methanol (5.0 mL) with 15% aqueous titanous chloride solution (5 mL, added in 1-mL portions over 1 h). The resultant mixture was stirred overnight and then treated with concentrated NH_4OH (15 mL). The mixture was then shaken with ether and filtered through Celite. The filter cake was thoroughly washed with ether. The combined ether phases were dried, and the solvent was removed to give a yellow oil, which was subjected to flash chromatography (45% CH_2Cl_2/light petroleum). After an unidentified impurity, the required amine (6%) was eluted as an oil: bp 70 °C [block] (0.07 mm); MS, *m/z* 147 (64%), 106 (100%); ^1H NMR δ 2.0–2.8 (m, 4 H), 3.43 (br s, 2 H), 4.7–5.2 (m, 2 H), 5.5–6.2 (m, 1 H), 6.4–7.1 (m, 4 H); ^{13}C NMR δ 30.8 (t), 32.9 (t), 115.2 (t), 115.8 (t), 118.9 (d), 126.1 (s), 127.2 (d), 129.6 (d), 138.3 (d), 144.4 (s); IR 3450, 3375, 1620, 995, 915 cm^{-1}. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90. Found: C, 81.44; H, 8.82. Further elution gave the para isomer (5%): bp 70 °C [block] (0.07 mm); MS, *m/z* 147 (16%, M^+), 106 (100%); ^1H NMR δ 2.0–2.8 (m, 4 H), 3.43 (s, 2 H), 4.7–5.2 (m, 2 H), 5.5–6.2 (m, 1 H), 6.48 and 6.87 (AA'BB' system, $J_{AB} \simeq J_{A'B'}$ = 8 Hz, 4 H); IR 3420, 3340, 1620, 825 cm^{-1}. Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90. Found: C, 81.31; H, 8.55.

***o*-Nitro-*N*-2-propenylacetanilide.** Powdered potassium hydroxide (26 g) and 3-bromopropene (17 g) were succesively added to a stirred solution of *o*-nitroacetanilide (21 g) in acetone (473 mL). The mixture was cautiously heated under reflux. After 3 min, the mixture was cooled, and the solvent was removed under reduced pressure. The residue was diluted with water and extracted three times with CH_2Cl_2. After the combined extracts had been washed with water and dried, the solvent was removed, and the residue was distilled to give the acetanilide (22.6 g, 88%): bp 134–135 °C (0.1 mm); MS, *m/z* 220 (6%, M^+), 105 (100%); ^1H NMR δ 1.87 (s, 2.4 H), 2.28 (s, 0.6 H), 3.7–5.5 (m, 4 H), 5.5–6.4 (m, 1 H), 7.3–8.2 (m, 4 H); IR 1670, 1530, 1350 cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49, N, 12.72. Found: C, 59.79; H, 5.67; N, 12.62.

***o*-Amino-*N*-2-propenylacetanilide.** The foregoing nitro compound was reduced with iron powder and water to give the corresponding amine (41%): mp 67–68 °C; MS, *m/z* 190 (83%, M^+), 119 (93%), 107 (100%); ^1H NMR δ 1.85 (s, 3 H), 3.77 (br s, 2 H), 3.85 and 4.29 (d of AB q, J_{AB} = 14 Hz, J_d = 6.5 Hz, 2 H), 4.8–5.3 (m, 2 H), 5.5–6.2 (m, 1 H), 6.4–7.3 (m, 4 H); IR (Nujol) 3400, 3340, 1635 cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42. Found: C, 69.54; H, 7.60.

***o*-Nitro-*N*-(2-methyl-2-propenyl)acetanilide.** This was prepared in 92% yield in the same manner as *o*-nitro-*N*-2-propenylacetanilide, except that 3-bromo-2-methylpropene was used as the alkylating agent. It was an oil: bp 152–156 °C (0.1–0.2 mm); ^1H NMR δ 1.75 (s, 3 H), 1.87 (s, 2.3 H), 2.21 (s, 0.7 H), 3.4–5.2 (m, 4 H), 7.1–8.0 (m, 4 H); IR 1670, 1525, 1355 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.5; H, 6.0. Found: C, 61.6; H, 6.3.

***o*-Amino-*N*-(2-methyl-2-propenyl)acetanilide.** Reduction of *o*-nitro-*N*-(2-methyl-2-propenyl)acetanilide with iron powder and water gave the amine (60%): mp 103.5–104.5 °C (from benzene/light petroleum); MS, *m/z* 204 (100%, M^+), 107 (94%); ^1H NMR δ 1.77 (s, 3 H), 1.84 (s, 3 H), 3.4–4.0 (m, 3 H), 4.4–4.9 (m, 3 H), 6.4–7.3 (m, 4 H); ^{13}C NMR δ 20.8 (q), 22.1 (q), 52.9 (t), 114.1 (t), 116.5 (d), 118.6 (d), 128.3 (s), 129.4 (d), 129.5 (d), 141.2 (s), 143.3 (s), 171.9 (s); IR 3390, 3360, 1635 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90, *m/z* 204.1263. Found: C, 70.65, H, 7.84, *m/z* 204.1261.

Diazonium Tetrafluoroborates. Method A. Sodium nitrite solution was added to the amine in cold 21% aqueous fluoroboric acid.[28] If necessary the crude product was recrystallized from acetone/ether.

Method B. Treatment of the amine with amyl nitrite and fluoroboric acid in ethanol/ether solution, as described by Cohen[29] for the diazotization of *o*-amino-*N*,*N*-dicyclohexylbenzamide, gave the required salt.

***o*-(2-Propynyloxy)benzenediazonium tetrafluoroborate (1c)**: method A; 75% yield; ^1H NMR (acetone-d_6) δ 3.47 (t, *J* = 2.5 Hz, 1 H), 5.38 (d, *J* = 2.5 Hz, 2 H), 7.5–8.0 (m, 2 H), 8.3–8.8 (m, 2 H); IR (Nujol) 3270, 3100, 2270, 1590, 1570, 1480, 1375, 1295, 1175, 1060, 995, 935, 765 cm^{-1}.

***o*-(*trans*-2-Butenyloxy)benzenediazonium tetrafluoroborate (1d)**: method A; 82% yield; ^1H NMR (acetone-d_6) δ 1.78 (d, *J* = 5.5 Hz, 3 H), 5.09 (d, *J* = 6 Hz, 2 H), 5.7–6.3 (m, 2 H), 7.4–7.9 (m, 2 H), 8.1–8.7 (m, 2 H); IR 3070, 2255, 1675, 1590, 1570, 1490, 1290, 1060, 755 cm^{-1}.

***o*-(1-Cyclopentenylmethoxy)benzenediazonium tetrafluoroborate (1e)**: method A; 82% yield; ^1H NMR (acetone-d_6) δ 1.7–2.7 (m, 6 H), 5.23 (s, 2 H), 6.02 (s, 1 H), 7.3–7.9 (m, 2 H), 8.2–8.5 (m, 1 H), 8.66 (d, *J* = 8 Hz, 1 H); IR (Nujol) 3100, 2270, 1600, 1570, 1495, 1450, 1300, 1270, 1060, 1000, 770 cm^{-1}.

***o*-(4-Pentenyloxy)benzenediazonium tetrafluoroborate (1j)**: method B; 62% yield; ^1H NMR (acetone-d_6) δ 1.8–2.6 (m, 4 H), 4.63 (t, *J* = 6.5 Hz, 2 H), 4.9–5.3 (m, 2 H), 5.6–6.3 (m, 1 H), 7.4–8.0 (m, 2 H), 8.2–8.8 (m, 2 H); IR (Nujol) 2280, 1640, 1600, 1570, 1080, 1020, 760 cm^{-1}.

***o*-[(2-Propenyloxy)carbonyl]benzenediazonium tetrafluoroborate (1k)**: method A, 93% yield; ^1H NMR (acetone-d_6) δ 5.09 (d, *J* = 6 Hz, 2 H), 5.3–5.8 (m, 2 H), 5.9–6.5 (m, 1 H), 8.2–8.8 (m, 3 H), 9.13 (dd, *J* = 8, 2 Hz, 1 H); IR (Nujol) 3110, 2290, 1725, 1450, 1300, 1060, 930, 795, 765 cm^{-1}.

***o*-(*N*,*N*-Di-2-propenylsulfamoyl)benzenediazonium tetrafluoroborate (1l)**: method A; 67% yield; ^1H NMR (acetone-d_6) δ 4.15 (d, 4 H), 5.0–5.5 (m, 4 H), 5.5–6.3 (m, 2 H), 8.2–8.7 (m, 3 H), 9.13 (d, *J* = 8 Hz, 1 H); IR (Nujol) 2276, 1562, 1363, 1314, 1176, 1160, 1062, 950, 892, 771 cm^{-1}.

***o*-(*N*-2-Propenylsulfamoyl)benzenediazonium tetrafluoroborate (1m)**: method A; 58% yield; ^1H NMR (acetone-d_6) δ 3.87 ("t", *J* = 5.5 Hz, 2 H), 4.9–5.5 (m, 2 H), 5.5–6.3 (m, 1 H), 7.63 (br s, 1 H), 8.2–8.9 (m, 3 H), 9.20 (d, *J* = 7 Hz, 1 H), IR (Nujol) 3300, 3100, 2300, 1640, 1565, 1430, 1355, 1195, 1075, 780, 775, 680 cm^{-1}.

3,5-Dichloro-2-(2-propenyloxy)benzenediazonium tetrafluoroborate (10): method A; 83% yield; ^1H NMR (acetone-d_6) δ 5.31 (d, *J* = 6 Hz, 2 H), 5.4–5.8 (m, 2 H), 6.1–6.6 (m, 1 H), 8.60 (d, *J* = 3 Hz, 1 H), 8.84 (d, *J* = 3 Hz, 1 H); IR (Nujol) 3080, 2280, 1275, 1155, 1069, 940, 865 cm^{-1}.

4-Nitro-2-(2-propenyloxy)benzenediazonium tetrafluoroborate (12a): method A; 66% yield; ^1H NMR (acetone-d_6) δ 5.38 (d, *J* = 6 Hz, 2 H), 5.4–5.9 (m, 2 H), 6.0–6.6 (m, 1 H), 8.2–8.6 (m, 2 H), 9.0 (d, *J* = 9 Hz, 1 H); IR (Nujol) 3135, 3100, 2295, 1620, 1580, 1545, 1360, 1320, 1280, 1065, 990, 820, 750 cm^{-1}.

2-(3-Butenyloxy)-4-nitrobenzenediazonium tetrafluoroborate (12b): method B; 49% yield; ^1H NMR (acetone-d_6) δ 2.6–3.0 (m, 2 H), 4.88 (t, *J* = 6.5 Hz, 2 H), 5.1–5.5 (m, 2 H), 5.8–6.4 (m, 1 H), 8.2–8.6 (m, 2 H), 9.02 (d, *J* = 9 Hz, 1 H); IR (Nujol) 3110, 2290, 1620, 1580, 1550, 1355, 1315, 1285, 1060, 920, 885, 820, 745 cm^{-1}.

***o*-(3-Butenyloxy)benzenediazonium Hexafluorophosphate (1i).** A solution of sodium nitrite (0.16 g) in water (0.68 mL) was added dropwise to a stirred mixture, which was cooled in ice, of *o*-(3-butenyloxy)aniline (0.33 g), water (3.3 mL), and concentrated

(28) Roe, A. *Org. React.* (*N. Y.*) **1949**, *5*, 193–228.
(29) Lipowitz, J.; Cohen, T. *J. Org. Chem.* **1965**, *30*, 3891–3894.

HCl (1.4 mL). After 30 min, 33% aqueous hexafluorophosphoric acid (0.54 mL) was added, and the mixture was stirred for 5 min. The precipitate was filtered and washed with ice-cold water. When the salt was nearly dry, it was washed with ether and then dried: IR (Nujol) 3110, 2270, 1600, 1575, 1495, 1460, 1305, 1150, 1080, 840, 770 cm^{-1}.

o-3-Butenylbenzenediazonium Hexafluorophosphate (1f). Diazotization of o-3-butenylaniline and subsequent addition of hexafluorophosphoric acid gave the hexafluorophosphate salt: ^1H NMR (acetone-d_6) δ 2.67 ("q", J = 7 Hz, 2 H), 3.40 (t, J = 7 Hz, 2 H), 5.0–5.3 (m, 2 H), 5.7–6.4 (m, 1 H), 7.8–8.6 (m, 3 H), 8.84 (d, J = 7.5 Hz, 1 H); IR (Nujol) 3100, 2260, 1460, 1590, 1560, 1050, 920, 840, 770, 760 cm^{-1}.

General Procedure for the Treatment of Diazonium Salts with Sodium Iodide. 3-(Iodomethyl)-2,3-dihydrobenzofuran (2a). A solution of **1a** (99 mg) in acetone (2.0 mL) was added to a stirred solution of sodium iodide (60 mg) in acetone (2.0 mL). The mixture was stirred for 15 min, after which time the solvent was removed under reduced pressure. Water was added to the residue, and the mixture was extracted twice with ether. The combined extracts were washed successively with water, 3% aqueous sodium thiosulfate solution, and brine. The dried extracts were concentrated to afford an oil, which was shown to be homogeneous by GLC (column B, 150 °C). A slight color was removed by either flash chromatography or preparative TLC (5% ether/light petroleum), and the resultant oil was distilled to afford **2a** (89 mg, 86%): bp 75 °C [block] (0.2 mm); n^{20}_D 1.6238; MS, m/z 260 (42%, M^+), 133 (100%); ^1H NMR δ 2.9–4.8 (m, 5 H), 6.6–7.3 (m, 4 H); ^{13}C NMR δ 8.9 (t), 45.0 (d), 77.9 (t), 110.5 (d), 121.0 (d), 124.6 (d), 129.1 (s), 129.6 (d), 160.6 (s); IR 1609, 1595, 1478, 1462, 1230, 965, 745 cm^{-1}. Anal. Calcd for C_9H_9IO: C, 41.56; H, 3.49. Found: C, 41.63; H, 3.70.

Reduction of 2a. A stirred solution of **2a** (100 mg) in dry THF (10 mL) was boiled overnight under reflux with lithium aluminum hydride (ca. 80 mg). The mixture was then cooled, and water (80 μL), 10% aqueous sodium hydroxide solution (80 μL), and water (240 μL) were successively added dropwise to the cooled mixture. After the mixture had been diluted with ether, it was filtered, and the residue was washed with ether. The combined filtrate and washings were then dried and concentrated to afford an oil, which was subjected to flash chromatography (hexane) to give pure **5a** (37 mg, 72%), identified by its ^1H NMR spectrum and GLC retention times (columns A and D, 150 °C), which were identical with those of an authentic sample.

3-(Iodomethyl)-3-methyl-2,3-dihydrobenzofuran (2b). A solution of **1b** (105 mg) was treated with sodium iodide as described above to give **2b** (98 mg, 89%) as an oil: bp 80 °C [block] (0.2 mm); n^{25}_D 1.6034; ^1H NMR δ 1.50 (s, 3 H), 3.35 (s, 2 H), 4.08 and 4.42 (AB q, J_{AB} = 9 Hz, 2 H), 6.5–7.4 (m, 4 H); ^{13}C NMR δ 18.1 (t), 25.4 (q), 45.9 (s), 83.1 (t), 110.5 (d), 120.9 (d), 122.8 (d), 129.3 (d), 131.9 (s), 159.8 (s); IR 1610, 1595, 1478, 1208, 1012, 975, 832, 746 cm^{-1}. Anal. Calcd for $C_{10}H_{11}IO$: C, 43.82; H, 4.05. Found: C, 43.53; H, 4.07. This compound was shown to be homogeneous by GLC (column C, 100 °C).

3-(Iodomethylene)-2,3-dihydrobenzofuran (8 and 9). After a solution of **1c** (98 mg) was treated with sodium iodide, a brown oil (93 mg, 90%) consisting of a 3:2 mixture of **8** and **9** was obtained. This mixture had two triplets (δ 79.8 and 77.4) and two doublets (δ 63.0 and 60.4) in the upper field region of the ^{13}C NMR spectrum. The two isomers were separated by preparative TLC (developed three times with petroleum ether). The component of higher R_f was eluted to give **8** as an oil, which decomposed spontaneously liberating fumes of iodine: ^1H NMR [obtained by subtracting the spectrum of **9** from that of the mixture] δ 4.85 (d, J = 3 Hz, 2 H), 6.28 (t, J = 3 Hz, 1 H), 6.6–7.4 (m, 4 H). The band of lower R_f was eluted to give **9** (30 mg, 29%) as an oil: MS, m/z 258 (77%, M^+), 131 (100%); ^1H NMR δ 4.97 (d, J = 2.5 Hz, 2 H), 5.95 (t, J = 2.5 Hz, 1 H), 6.6–7.4 (m, 3 H), 8.25 (dd, J = 8, 1 Hz, 1 H); exact mass calcd for C_9H_7OI m/z 257.954, found m/z 257.954.

5,7-Dichloro-3-(iodomethyl)-2,3-dihydrobenzofuran (11). A solution of **10** was treated with sodium iodide in the usual way. After purification by TLC (20% ether/light petroleum), **11** (114 mg, 87%) was obtained as a light yellow oil, which crystallized on standing. A small portion was distilled: bp 90 °C [block] (0.2 mm); mp 29–31 °C; n^{32}_D 1.6354; MS, m/z 332 (M^+), 330 (M^+), 328 (M^+); ^1H NMR δ 2.9–5.0 (m, 5 H), 7.0–7.2 (m, 2 H); ^{13}C NMR δ 7.2 (t), 45.4 (d), 79.0 (t), 123.4 (d), 126.1 (s), 129.6 (d), 132.2 (s), 155.8 (s); IR (CCl_4) 1602, 1592, 1471, 1451, 1197, 1158, 968, 858 cm^{-1}. Anal. Calcd for $C_9H_7Cl_2IO$: C, 32.86; H, 2.14. Found: C, 33.26; H, 2.44.

3-(Iodomethyl)-6-nitro-2,3-dihydrobenzofuran (13a). A solution of **12a** in acetone was treated with sodium iodide. After the usual workup and chromatography (45% CH_2Cl_2/hexane), **13a** (84%) was obtained: mp 116–117 °C (from toluene/light petroleum); MS, m/z 305 (34%, M^+), 177 (100%); ^1H NMR δ 3.0–3.5 (m, 2 H), 3.5–4.1 (m, 1 H), 4.2–5.0 (m, 2 H), 7.0–7.9 (m, 3 H); ^{13}C NMR δ 7.0 (t), 44.2 (d), 79.1 (t), 104.1 (s), 105.8 (d), 116.7 (d), 124.6 (d), 137.5 (s), 161.3 (s); IR (Nujol) 1520, 1350, 975, 750 cm^{-1}. Anal. Calcd for $C_9H_8INO_3$: C, 35.43; H, 2.64; m/z 304.9551. Found: C, 35.34; H, 2.80; m/z 304.9548.

Reaction of 1d with Sodium Iodide. After the usual workup, a brown oil was obtained, which was shown by GLC (column B, 150 °C) to consist of two components in the ratio 64:36. This oil was subjected to preparative TLC (developed twice with 10% ether/light petroleum). The component of higher R_f was distilled to afford one diastereoisomer of **2d** (26%) as an oil: bp 60 °C [block] (0.25 mm); MS, m/z 274 (55%, M^+), 119 (100%), 91 (99%); ^1H NMR (CCl_4) δ 1.63 (d, J = 7 Hz, 3 H), 3.8–4.4 (m, 2 H), 4.4–4.7 (m, 2 H), 6.6–7.3 (m, 4 H); IR 1606, 1594, 1477, 1228, 828 cm^{-1}. Anal. Calcd for $C_{10}H_{11}IO$: C, 43.82; H, 4.05. Found: C, 44.03; H, 4.11. The band of lower R_f was eluted and distilled to give the other diastereoisomer of **2d** (47%): mp 31–33 °C; bp 60 °C [block] (0.4 mm); MS, m/z 274 (5%, M^+), 91 (100%); ^1H NMR (CCl_4) δ 1.93 (d, J = 7 Hz, 3 H), 3.4–3.8 (m, 1 H), 4.0–4.7 (m, 3 H), 6.5–7.4 (m, 4 H); IR (CCl_4) 1607, 1595, 1477, 1230, 830 cm^{-1}. Anal. Calcd for $C_{10}H_{11}IO$: C, 43.82; H, 4.05. Found: C, 43.93; H, 4.28.

Reduction of 2d. Lithium aluminum hydride (ca. 11 mg) was added to a stirred solution of the foregoing diastereoisomers (**2d**) (81 mg) in dry ether (5.0 mL). The mixture was boiled under reflux for 24 h. Water (11 μL), 10% aqueous sodium hydroxide solution (11 μL), and water (33 μL) were then successively added dropwise, and the resultant mixture was stirred for 5 min and then filtered. The solvent was removed under reduced pressure from the dried filtrate to give 3-ethyl-2,3-dihydrobenzofuran (**5d**) (39.5 mg, 90%) as an oil, which was homogeneous by GLC (columns A, B, and D, 150 °C) and had the same retention time and ^1H NMR spectrum as a sample obtained from tributyltin hydride reduction of **1d**.[1] A small sample was purified by flash chromatography and distilled: bp 105 °C [block] (18 mm) [lit.[30] bp 100–102 °C (18 mm)]; n^{26}_D 1.5244 [lit.[30] n^{26}_D 1.5240].

2,3-Dihydrobenzofuran-3-spiro-(2'-iodocyclopentane) (14). **1e** was treated in the usual way with sodium iodide to afford **14** (73%): mp 75.5–76.5 °C (from light petroleum, low temperature); MS, m/z 300 (30%, M^+), 131 (100%); ^1H NMR δ 1.5–2.9 (m, 6 H), 4.0–4.4 (unresolved, 1 H), 4.24 and 4.66 (AB q, J_{AB} = 9 Hz, 2 H), 6.6–7.3 (m, 4 H); ^{13}C NMR δ 22.7 (t), 35.6 (t), 37.3 (t), 39.2 (d), 57.9 (s), 83.5 (t), 110.1 (d), 120.9 (d), 122.6 (d), 129.3 (d), 130.6 (s), 160.5 (s); IR (Nujol) 1600, 1480, 1225, 835, 765 cm^{-1}. Anal. Calcd for $C_{12}H_{13}IO$: C, 48.02; H, 4.37. Found: C, 47.70; H, 4.68.

2,3-Dihydrobenzofuran-3-spirocyclopentane (15). A stirred solution of **14** was deiodinated with $LiAlH_4$ as described for **2a**. The crude reaction product was subjected to flash chromatography to afford **15** (71%) as an oil: MS, m/z 174 (46%, M^+), 132 (100%), 131 (90%); ^1H NMR δ 1.80 (br "s", 8 H), 4.23 (s, 2 H), 6.5–7.2 (m, 4 H); ^{13}C NMR δ 25.1 (t), 40.1 (t), 53.0 (s), 84.5 (t), 109.6 (d), 120.7 (d), 122.8 (d), 128.0 (d), 135.6 (s), 160.8 (s). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.58; H, 7.91. This compound was shown to be >98% pure by GLC (column C, 100 °C).

1-(Iodomethyl)indane (2f). A solution of o-3-butenylbenzenediazonium hexafluorophosphate (**1f**) (116 mg) in acetone (2.0 mL) was added to a stirred solution of sodium iodide (60 mg) in acetone (2.0 mL). After the mixture had been stirred for 15 min, it was subjected to the usual workup. GLC analysis (column C, 125 °C) revealed the presence of two components in the ratio 85:15. The major compound, obtained in pure form by flash chromatography (light petroleum) was **2f** (68 mg, 66%): bp 80

(30) Cologne, J.; Descotes, G. *Bull. Soc. Chim. Fr.* **1959**, 817–819.

°C [block] (0.3 mm); $n^{22.5}_D$ 1.6510; MS, m/z 258 (4%, M^+), 131 (100%); ^1H NMR δ 1.4–3.7 (m, 7 H), 7.08 (br "s", 4 H); ^{13}C NMR δ 12.1 (t), 30.7 (t), 33.4 (t), 47.5 (d), 124.0 (d), 125.2 (d), 126.6 (d), 127.6 (d), 144.5 (s), 144.8 (s); IR 1470, 1450, 1160, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{11}I$: C, 46.54; H, 4.30. Found: C, 46.72; H, 4.42. The minor component was **3f**, identified by its ^1H NMR spectrum and GLC retention time, which were identical with those of an authentic specimen.[13]

4-(Iodomethyl)chroman (2i). A solution of **1i** (BF_4^- salt) was treated with sodium iodide in acetone in the usual manner. After workup and flash chromatography (10% CH_2Cl_2/light petroleum) **2i** (65%) was obtained: mp 33–34 °C; ^1H NMR δ 1.9–2.3 (m, 2 H), 2.9–3.8 (m, 3 H), 3.9–4.3 (m, 2 H), 6.6–7.4 (m, 4 H); ^{13}C NMR δ 12.1 (t), 27.6 (t), 36.1 (d), 62.6 (t), 117.2 (d), 120.6 (d), 123.6 (s), 128.5 (d), 129.3 (d), 154.6 (s); IR 1600, 1575, 1480, 1265, 1215, 1165, 1015, 760, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{11}IO$: C, 43.82; H, 4.05. Found: C, 43.76; H, 4.16. The reaction was repeated using the hexafluorophosphate salt. The crude reaction product was examined by GLC (column C, 150 °C) to reveal two components in the ratio 94:6. The major component was **2i** (85%), isolated by flash chromatography (20% CH_2Cl_2/light petroleum). Its physical properties (^1H NMR and IR spectra, GLC retention time) were identical with those measured on the sample prepared above. The minor component was **3i** (5%), which had a GLC retention time (column C, 150°C) and ^1H NMR spectrum identical with those of an authentic sample.[13]

Reaction of 12b with Sodium Iodide. Two compounds were obtained after workup and flash chromatography (40% CH_2Cl_2/light petroleum). The first eluted was 2-(3-butenyloxy)-1-iodo-4-nitrobenzene (**12c**) (8%): mp 50–51 °C (from light petroleum, low temperature); MS, m/z 319 (46%, M^+), 63 (100%); ^1H NMR δ 2.60 (q, J = 7 Hz, 2 H), 4.15 (t, J = 7 Hz, 2 H), 4.9–5.4 (m, 2 H), 5.6–6.4 (m, 1 H), 7.2–7.8 (m, 2 H), 7.95 (d, J = 9 Hz, 1 H). Anal. Calcd for $C_{10}H_{10}INO_3$: C, 37.64; H, 3.16. Found: C, 37.91; H, 3.43. Further elution gave 4-(iodomethyl)-7-nitrochroman (**13b**) (83%): mp 113.5–114 °C (from CH_2Cl_2/light petroleum); MS, m/z 319 (30%, M^+), 192 (100%); ^1H NMR δ 1.9–2.4 (m, 2 H), 2.9–3.8 (m, 3 H), 4.18 (t, J = 5 Hz, 2 H), 7.1–7.8 (m, 3 H); ^{13}C NMR δ 10.1 (t), 27.2 (t), 36.0 (d), 63.4 (t), 112.7 (d), 115.1 (d), 130.0 (d), 130.8 (d), 152.2 (s); IR (Nujol) 1520, 1360, 1335, 1020, 880, 740 cm^{-1}. Anal. Calcd for $C_{10}H_{10}INO_3$: C, 37.64; H, 3.16. Found: C, 37.37; H, 3.32.

1-Acetyl-3-(iodomethyl)indoline (2g). Treatment of **1g** with sodium iodide gave **2g** (84%): mp 85.5–86.5 °C (from light petroleum); MS, m/z 301 (78%, M^+), 118 (100%); ^1H NMR δ 2.03 (s, 3 H), 2.9–4.4 (m, 5 H), 6.7–7.3 (m, 3.2 H), 8.05 (br, d, 0.8 H); ^{13}C NMR δ 10.0 (t), 24.3 (q), 42.8 (d), 56.4 (t), 117.6 (d), 124.0 (d), 129.2 (d); IR 1660, 1590, 1480, 1400, 760 cm^{-1}. Anal. Calcd for $C_{11}H_{12}INO$: C, 43.88; H, 4.02; m/z 300.9962. Found: C, 43.77; H, 4.12; m/z 300.9965.

1-Acetyl-3-(iodomethyl)-3-methylindoline (2h). 1h (364 mg) was treated with sodium iodide (180 mg) to give after flash chromatography (CH_2Cl_2) crude **2h** (316 mg) (>75% pure): ^1H NMR δ 1.48 (s, 3 H), 2.20 (s, 3 H), 3.30 (s, 2 H), 3.65 and 3.99 (AB q, J_{AB} = 11 Hz, 2 H), 6.7–7.4 (m, 3.2 H), 8.07 (br d, 0.8 H); ^{13}C NMR δ 18.9 (t), 24.3 (q), 26.5 (q), 44.3 (s), 62.4 (t), 117.7 (d), 122.4 (d), 124.1 (d), 129.2 (d), 136.1 (s), 143.0 (s), 168.8 (s).

A ^{13}C NMR absorption at δ 65.5, assigned to an impurity, was less than 15% of the intensity of the resonance at δ 62.4. Further purification of this indoline was difficult. By repeated recrystallization (light petroleum, low temperature) a small sample of purity >97% by GLC was obtained: MS, m/z 315 (45%), 146 (96%), 132 (100%). Anal. Calcd for $C_{12}H_{14}INO$: C, 45.73; H, 4.48. Found: C, 46.63; H, 4.69.

Reaction of 1j with Sodium Iodide. After the usual workup and flash chromatography (5% CH_2Cl_2/light petroleum) **3j** (60%) was obtained. It was shown by GLC and ^1H NMR spectroscopy to be identical with the sample prepared below.

***o*-(4-Pentenyloxy)iodobenzene (3j).** A mixture of *o*-iodophenol (440 mg), water (2.0 mL), sodium hydroxide (80 mg), and 5-bromopentene (325 mg) was boiled under reflux for 5 h. The cooled reaction mixture was then diluted with water and extracted twice with ether. The combined ether layers were washed with sodium hydroxide solution and water, concentrated, and distilled to afford **3j** (31 mg, 61%): bp 120 °C [block] (0.2 mm); $n^{22.5}_D$ 1.5755; MS, m/z 288 (44%, M^+), 220 (100%); ^1H NMR δ 1.4–2.4 (m, 4 H), 3.83 (t, 2 H), 4.7–5.2 (m, 2 H), 5.4–6.2 (m, 1 H), 6.4–6.9 (m, 2 H), 6.9–7.3 (m, 1 H), 7.63 (dd, J = 8, 2 Hz, 1 H); IR 3070, 1640, 1585, 1480, 1460, 1440, 1280, 1255, 1055, 1020, 920, 755 cm^{-1}. Anal. Calcd for $C_{11}H_{13}IO$: C, 45.86; H, 4.55. Found: C, 45.91; H, 4.64.

2-Propenyl *o*-Iodobenzoate (3k). (a) **1k** (1.11 g) was treated with sodium iodide in the usual way to afford **3k** (750 mg, 66%), which was identical [refractive index, ^1H NMR, IR spectrum, GLC retention time (column C, 150 °C)] with the sample prepared below.

(b) Thionyl chloride (2.0 mL) was slowly added to *o*-iodobenzoic acid (496 mg). The stirred mixture was then boiled under reflux for 30 min. After this period, the excess thionyl chloride was removed under reduced pressure. A solution of allyl alcohol (139 mg) in pyridine (0.5 mL) was added slowly with external cooling to a stirred solution of the residue in pyridine (4.0 mL). When the addition was complete, the mixture was stirred for 2 h, diluted with water, and extracted three times with ether. After the combined ether extracts were successively washed with water, 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine, the dried organic layer was distilled to afford **3k** (320 mg, 56%): bp 105 °C [block] (0.5 mm); n^{25}_D 1.5890; MS, m/z 288 (18%, M^+), 231 (100%); ^1H NMR δ 4.73 (d, J = 6 Hz, 2 H), 5.1–5.5 (m, 2 H), 5.7–6.5 (m, 1 H), 7.0–8.1 (m, 4 H); IR (CCl_4) 2990, 1730, 1425, 1285, 1130, 1095, 905, 870 cm^{-1}. Anal. Calcd for $C_{10}H_9IO_2$: C, 41.69; H, 3.15. Found: C, 41.77; H, 3.35.

Reaction of 1l with Sodium Iodide. Two compounds were obtained after workup and chromatography (8% EtOAc/light petroleum). The first compound eluted was 4-iodo-*N*-2-propenyl-2,3,4,5-tetrahydrobenzo[*f*]-1,2-thiazepine 1,1-dioxide (**4l**) (310 mg, 57%): mp 94.5–95.5 °C (from bp 80–100 °C petroleum ether); MS m/z 363 (6%, M^+), 236 (100%); ^1H NMR δ 3.0–4.7 (m, 7 H), 5.0–5.4 (m, 2 H), 5.4–6.1 (m, 1 H), 7.1–7.6 (m, 3 H), 7.8–8.2 (m, 1 H); ^{13}C NMR δ 21.0 (d), 47.7 (t), 50.3 (t), 56.8 (t), 119.5 (t), 117.7 (d), 128.9 (d), 132.5 (d), 132.8 (d), 133.2 (d), 137.8 (s), 146.5 (s); IR (Nujol) 3025, 1348, 1166, 1012, 936, 907, 693 cm^{-1}. Anal. Calcd for $C_{12}H_{14}INO_2S$: C, 39.68; H, 3.89; N, 3.86. Found: C, 39.50; H, 4.01; N, 3.74. Further elution afforded 4-(iodomethyl)-*N*-2-propenyl-3,4-dihydro-2*H*-benzo[*e*]-1,2-thiazine 1,1-dioxide (**2l**) (107 mg, 20%): mp 88.5–90.5 °C (from bp 80–100 °C petroleum ether); MS, m/z 363 (2%, M^+), 236 (100%); ^1H NMR δ 3.0–4.4 (m, 7 H), 5.1–5.6 (m, 2 H), 5.6–6.4 (m, 1 H), 7.1–7.7 (m, 3 H), 7.7–8.1 (m, 1 H); ^{13}C NMR δ 7.7 (t), 38.6 (d), 49.4 (t), 49.9 (t), 120.6 (t), 124.7 (d), 128.6 (d), 129.2 (d), 132.6 (d), 136.4 (s), 137.1 (s), 145.3 (s); IR (CCl_4) 3025, 1350, 1316, 1166, 1133, 982, 925, 912, 688 cm^{-1}. Anal. Calcd for $C_{12}H_{14}INO_2S$: C, 39.68; H, 3.89; m/z 362.9791. Found: C, 39.58; H, 3.97; m/z 362.9794.

Reaction of 1m with Sodium Iodide. The crude reaction mixture was subjected to flash chromatography (10% EtOAc/light petroleum). The first compound eluted was 4-iodo-2,3,4,5-tetrahydrobenzo[*f*]-1,2-thiazepine 1,1-dioxide (**4m**) (50%): mp 122–134 °C (from CH_2Cl_2/light petroleum) [A sharp mp could not be obtained even after repeated recrystallization]; MS, m/z 323 (2%, M^+), 196 (100%); ^1H NMR (acetone-d_6) δ 3.4–4.3 (m, 4 H), 4.4–4.9 (m, 1 H), 6.6–7.1 (br, 1 H), 7.3–7.7 (m, 3 H), 7.8–8.1 (m, 1 H); ^{13}C NMR (acetone-d_6) δ 28.3 (d), 45.5 (t), 53.9 (t), 127.4 (d), 127.6 (d), 132.9 (d), 133.1 (d), 136.5 (s), 142.8 (s); IR (Nujol) 3270, 1445, 1325, 1160, 1065, 830, 770, 740, 720 cm^{-1}. Anal. Calcd for $C_9H_{10}INO_2S$: C, 33.45; H, 3.12; m/z 322.9479. Found: C, 33.33; H, 3.12; m/z 322.9476. Further elution afforded 4-(iodomethyl)-3,4-dihydrobenzo[*e*]-1,2-thiazine 1,1-dioxide (**2m**) (23%): mp 129–130 °C (from CH_2Cl_2/light petroleum); MS, m/z 323 (2%, M^+), 196 (100%), 103 (91%); ^1H NMR (acetone-d_6) δ 3.0–3.4 (m, 1 H), 3.5–4.0 (m, 4 H), 6.57 (br s, 1 H), 7.2–7.9 (m, 4 H); ^{13}C NMR (acetone-d_6) δ 9.5 (t), 39.0 (d), 46.9 (t), 125.0 (d), 129.2 (d), 131.1 (d), 133.2 (d), 138.1 (s), 139.6 (s); IR (Nujol) 3250, 1415, 1315, 1190, 1170, 840, 770, 715 cm^{-1}. Anal. Calcd for $C_9H_{10}INO_2S$: C, 33.45; H, 3.12; m/z 322.9479. Found: C, 33.78; H, 3.10; m/z 322.9476.