

less steric crowding than in the alternatives.

In summary, a direct S_H2 mechanism³⁷ appears highly unlikely for the radicals studied here. Radical addition to one of the double bonds followed by reductive elimination appears most likely, although a six-coordinate *cis*-bis(alkyl)cobalt(IV) intermediate

(37) We would also consider that reaction occurs by displacement at cobalt, not carbon ($R^{\bullet} + R'Co(dmgH)_2 \rightarrow RCo(dmgH)_2 + R'^{\bullet}$). To retain the product specificity, however, this would require that displacement from CrR^{2+} occur more rapidly at carbon ($R^{\bullet} + R'Cr^{2+} \rightarrow RR' + Cr^{2+}$) than at chromium ($R^{\bullet} + R'Cr^{2+} \rightarrow R'^{\bullet} + CrR^{2+}$), else cross-coupled products would be seen. We tend to discount this, therefore, in light of the fortuitous combinations of rate constants needed.

remains a possibility. The failure of $PhCH_2^{\bullet}$ to react with the organocobaloximes is probably related to the stability of this radical.

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Supplementary Material Available: Tables of kinetic data from individual competition experiments (4 pages). Ordering information is given on any current masthead page.

Formation of Functionalized Dihydrobenzofurans by Radical Cyclization¹

Gordon F. Meijs* and Athelstan L. J. Beckwith*†

Contribution from the Department of Organic Chemistry, The University of Adelaide, Adelaide, S.A. 5001, Australia, and Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. Received December 30, 1985

Abstract: Treatment of the arenediazonium tetrafluoroborates **4a** and **4b** in Me_2SO solution with copper(II) bromide or chloride gave the cyclized halo compounds **5a**, **5b**, and **5c** in good yield. Copper(I) cyanide/pyridine effected ring closure of **4b** to afford the nitrile **5d**. Dihydrobenzofuran derivatives were also formed on treatment of **4a** or **4b** with benzenethiolate or butanethiolate ion in Me_2SO . Chain mechanisms involving cyclization of an intermediate aryl radical are suggested.

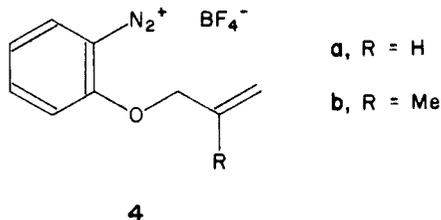
Aryl radicals with ortho substituents containing double bonds in the 5,6 or 6,7 positions relative to the radical center undergo rapid, regioselective cyclization (**1** \rightarrow **2**) in the *exo* mode.²⁻⁴

Previously, such radicals had been generated for kinetic studies by treating the appropriate aryl iodide with tri-*n*-butyltin hydride.³ This procedure, however, was unattractive for preparative work since reaction mixtures needed to be dilute to ensure the predominance of the cyclized product, complete removal of the tin compounds was difficult,⁵⁻⁷ initiation was unreliable, and the considerable quantity of tributyltin hydride required was expensive.

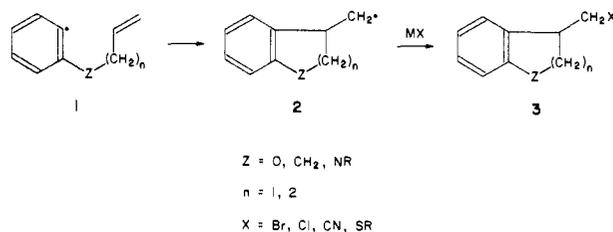
We sought, therefore, alternative methods for effecting the ring closure of suitable aryl radicals. Procedures which were likely both to generate the radical and to introduce a new functional group (X) at the cyclized radical center (Scheme I) were of especial interest. Such reactions would afford functionalized products (e.g., **3**) suitable for further elaboration.

The radical precursors chosen for study were diazonium tetrafluoroborates. A large number of reactions involving diazonium salts are thought to involve free-radical intermediates,⁸⁻¹⁰ and the tetrafluoroborate salts are easily prepared, are relatively stable, and are convenient to handle and purify.

This paper describes ring closures of *o*-(2-propenyloxy)-benzenediazonium tetrafluoroborate (**4a**) and *o*-((2-methyl-2-propenyl)oxy)benzenediazonium tetrafluoroborate (**4b**) induced by thiodediazotiation agents and copper-based "Sandmeyer" dediazotiation reagents.



Scheme I



Results and Discussion

Bromodediazotiation. Initial exploratory experiments employing copper(I) bromide were unsuccessful and gave cyclized material in only low yield accompanied by much intractable tarry material. Consequently, we turned to a method involving the use of copper(II) bromide in Me_2SO .¹¹ This procedure is an efficient modification of conventional Sandmeyer conditions and is espe-

(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.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593-600.

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(4) For a discussion of the regioselectivity of radical ring closures, see: Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482-483.

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(6) Berge, J. M.; Roberts, S. M. *Synthesis* **1979**, 471-472.

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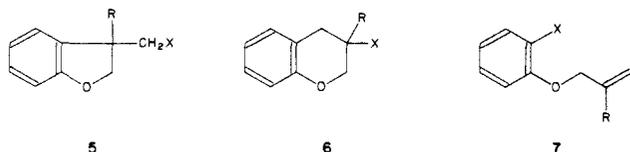
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(11) Kobayashi, M.; Yamada, E.; Matsui, M.; Kobori, N. *Org. Prep. Proced.* **1969**, *1*, 221-224.

† Current address: Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia.

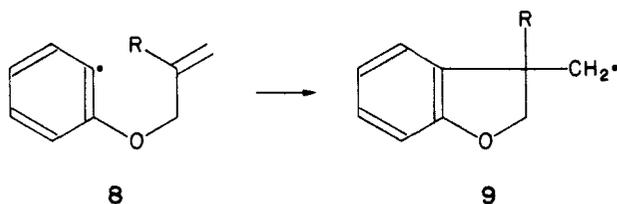
cially suited to diazonium tetrafluoroborates,¹¹ which are generally only sparingly soluble in aqueous media.

The cyclized bromo compound **5b** was isolated in 89% yield, when a solution of *o*-(2-methyl-2-propenyl)oxybenzenediazonium tetrafluoroborate (**4b**) was stirred at room temperature for 15 h with copper(II) bromide in Me₂SO. Similarly, the diazonium salt **4a** gave the cyclized (bromomethyl)dihydrobenzofuran **5a** in 82% yield. The structure of **5a** was established by ¹³C NMR spectroscopy and confirmed by treating a small portion of the product with tri-*n*-butyltin hydride; the resultant product was identical with an authentic sample of 3-methyl-2,3-dihydrobenzofuran.²

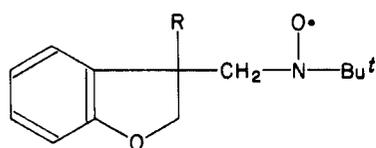


- | | |
|--------------------|-----------------------------------|
| a, R = H, X = Br | f, R = Me, X = N ₂ SPh |
| b, R = Me, X = Br | g, R = H, X = SPh |
| c, R = Me, X = Cl | h, R = Me, X = SBU |
| d, R = Me, X = CN | i, R = Me, X = SCSOEt |
| e, R = Me, X = SPh | j, R = Me, X = SH |

It is noteworthy that the reaction mixtures from **4a** and **4b** were not contaminated with products **6a** and **6b** derived from cyclization in the endo mode. This is consistent with the high regioselectivity previously observed for the intramolecular addition of aryl radicals to form medium-sized rings.³ It is also noteworthy that neither reaction mixture contained the uncyclized products **7a** or **7b**. This observation accords with the high rates of cyclization of the corresponding aryl radicals **8a** and **8b**. Recent data¹² give rate constants for exo ring closure of **8a** and **8b** to give **9a** or **9b** at 20 °C of 4.8×10^9 and 1.5×10^9 s⁻¹, respectively. Consequently, any bimolecular process leading to products such as **7a** or **7b** will not compete effectively with ring closure unless its rate constant is approximately diffusion controlled ($k \approx 10^9$ M⁻¹ s⁻¹) and the concentration of the second reagent (copper(II) bromide in this case) is ≥ 1 M.

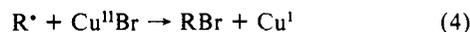
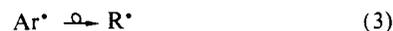
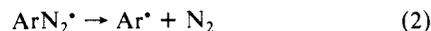
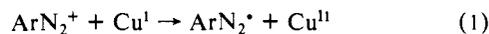


- a, R = H
b, R = Me



- 10 a, R = H
b, R = Me

We visualize that the reactions follow a radical chain mechanism, the propagation steps of which are outlined in eq 1–4, where ArN₂⁺ represents the diazonium ion of **4a** or **4b** and R• represents a cyclized radical **9a** or **9b**.



Such a mechanism has salient features similar to those originally postulated by Kochi^{13,14} for the Sandmeyer and Meerwein arylations. In eq 4, the copper(II) bromide undergoes a ligand transfer to the cyclized radical **9** to afford the observed bromo compound. In doing so, it is reduced to copper(I), which can then generate a new radical from the diazonium salt by electron transfer (eq 1). During the reaction, the copper(II) bromide, the ligand-transfer or chain-propagating agent, is in relatively high concentration. We believe that this contributes to the overall efficiency of the reaction. It is likely that the reaction is initiated by traces of copper(I) in the copper(II) bromide.

The solvent had a marked effect on the reaction yield. For example, when acetone was substituted for Me₂SO, the yield of the bromo compound **5a** was halved and the reaction mixture was contaminated with tars. We are unsure as to the reason; possibly the increase in the Cu^{II}/Cu^I redox potential when Me₂SO is used as solvent facilitates chain propagation by bromine transfer (eq 4).¹⁵

Chlorodediazoniatio. Ring closure of the diazonium salt **4b** was similarly attempted under conditions reported for chlorodediazoniatio.¹¹ After a solution of the diazonium salt **4b** and copper(II) chloride in Me₂SO had been stirred overnight, 3-(chloromethyl)-3-methyl-2,3-dihydrobenzofuran (**5c**) was isolated in 63% yield. Neither the uncyclized aryl chloride **7c** nor the product of cyclization in the endo mode **6c** was found in the reaction mixtures. We take the mechanism as being analogous to that in eq 1–4. Evidently, for the reasons outlined above, interception of the uncyclized aryl radical **8b** by copper(II) chloride cannot compete with cyclization.

Cyanodediazoniatio. The copper(I) cyanide/sodium cyanide complex in Me₂SO has been reported to effect cyanodediazoniatio with moderate efficiency.¹¹ However, only tars were isolated when the diazonium salt **4b** was treated with this combination of reagents. Several other attempts, including stirring with copper(I) cyanide in Me₂SO and more traditional Sandmeyer cyanodediazoniatio conditions,¹⁶ failed to give identifiable products. When, however, a solution of the diazonium salt **4b** in Me₂SO was treated for 10 min with a pyridine solution of copper(I) cyanide, the nitrile **5d** was formed in 40% yield. The remainder of the mixture was intractable. The yield of the nitrile **5d** was not improved by carrying out the reaction for a longer time. We suggest that the function of the pyridine is to stabilize the copper(I) oxidation state¹⁵ and thus facilitate ligand transfer from a copper(II) cyanide species to the radical. Pyridine has also been reported to catalyze certain homolytic dediazoniatio.^{17–19}

Thiodediazoniatio. Alkanethiolate ions have been reported to be effective reagents for (alkylthio)dediazoniatio of arenediazonium salts.²⁰ Although arenethiolates undergo a similar reaction, diazo sulfide formation frequently competes effectively.²⁰ We sought to determine whether thiolate ions would be effective reagents for inducing ring closure of the diazonium salt **4b**. Possible outcomes of the reaction include direct thiodediazoniatio to give **7e**, diazo sulfide (**7f**) formation, and cyclization with incorporation of a thioether group to afford **5e** or **6e**.

Nitrogen was rapidly evolved when the diazonium salt **4b** was added to a solution of sodium benzenethiolate in Me₂SO. The

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(15) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 798. Parker, A. J.; Clarke, D. A.; Couche, R. A.; Miller, G.; Tilley, R. I.; Waghorne, W. E. *Aust. J. Chem.* **1977**, *30*, 1661.

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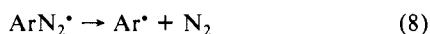
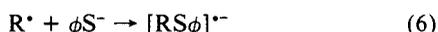
(20) Price, C. C.; Tsunawaki, S. *J. Org. Chem.* **1963**, *28*, 1867–1868.

(12) Johnston, L. J.; Luszyk, J.; Wayner, D. D. M.; Abeywickrema, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596. Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464–465.

product, isolated in 60% yield, was the cyclized thioether **5e**. It was accompanied by some unidentified tarry material, which could be removed readily by chromatography on silica gel. Similarly, the diazonium salt **4a**, on reaction with benzenethiolate ion, afforded the cyclized thioether **5g** in 53% yield. The addition of copper powder to the reaction mixture had no effect on the yield.

When the reaction was repeated with alkanethiolates, alkylthioethers were formed, but the yields were lower unless the reaction was carried out in the presence of copper powder. Thus, when a Me_2SO solution of sodium *n*-butanethiolate and the diazonium salt **4b** were stirred together, the thioether **5h** was formed in 43% yield. When the reaction was repeated in the presence of copper powder, the yield was raised to 64%.

A free-radical chain mechanism with propagation steps shown in eq 5–8, where ϕS^\cdot represents either an alkanethiolate or an arenethiolate anion, is consistent with the experimental results.



This mechanism is essentially a modification of the general $\text{S}_{\text{RN}}1$ reaction scheme^{21–23} with an intermediate cyclization step. Radical anion intermediates, $[\text{ArSR}]^\cdot$, have been proposed for the reaction of aryl radicals with alkanethiolate ions.²⁴ Initiation is likely to proceed via spontaneous electron transfer from the thiolate ion to the diazonium salt.²⁵ In the case of butanethiolate, which is a less effective reducing agent than benzenethiolate, the copper powder is envisaged to play a role in improving the initiation of the reaction.

We reject reaction pathways involving cage decomposition of the diazo sulfide intermediate **7f**,²⁵ since products were not found resulting from interception of the aryl radical before cyclization.

Attempts to extend the scope of the reaction using sodium hydrosulfide as a reagent for thiodediazotiation failed. Nevertheless, we were able to prepare an *S*-aryl *O*-ethyl dithiocarbonate, which could readily be converted into the corresponding thiol. Reaction of the diazonium salt **4b** with potassium *O*-ethyl dithiocarbonate (potassium ethyl xanthate)²⁶ in acetone gave the cyclized dithiocarbonate **5i** in 75% yield. The thiol **5j** could be obtained in 77% yield by treatment of the dithiocarbonate **5i** with 1,2-diaminoethane.

Potassium ethyl xanthate was also effective in generating aryl radicals for ESR spin trapping experiments. When nitrosoisobutane and a solution of **4b** in acetone were mixed, an ESR signal did not appear until a trace of xanthate ion was added. The resultant spectrum, a_{H} (1) 5.50, a_{H} (1) 15.75, and a_{N} 15.25 G, was that attributable to the spin adduct **10b**. Similarly, when the diazonium salt **4a** was treated in acetone solution with potassium ethyl xanthate and nitrosoisobutane, a strong ESR signal, a_{H} (1) 11.38, a_{H} (1) 13.25, and a_{N} 15.50 G, ascribed to the nitroxyl radical **10a**, was obtained.

Experimental Section

General Methods. Elemental analyses were carried out by the Australian Microanalytical Service, Melbourne. IR spectra were recorded on a Perkin-Elmer 397 spectrometer. ¹H NMR spectra were determined unless otherwise stated in CDCl_3 solution relative to Me_4Si on either a JEOL JNM-PMX60 or a Varian T-60 spectrometer operating at 60 MHz. ¹³C NMR spectra were recorded using CDCl_3 as solvent on a Bruker WP-80DS spectrometer operating at 20.1 MHz. Mass spectra were determined on either a Hitachi Perkin-Elmer RMU-7D spectrom-

eter or an AEI-MS 3074, both operating at 70 eV. ESR spectra were recorded on a Varian E-9 spectrometer. GLC was conducted on either a Perkin-Elmer 881 chromatograph (column A) or a Pye 104 GLC (column B). The columns used were as follows: column A, 1.5 m \times 3.2 mm, 15% SE-30 on Varaport 30 (80–100 mesh); column B, 1.5 m \times 3.2 mm, 1% SE-30 on Varaport 30 (100–120 mesh).

Starting Materials. *o*-(2-Propenyloxy)benzenediazonium tetrafluoroborate (**4a**) and *o*-((2-methyl-2-propenyl)oxy)benzenediazonium tetrafluoroborate (**4b**) were prepared as previously described.² Me_2SO was distilled from calcium hydride and stored over 4-Å molecular sieves under an atmosphere of nitrogen. Benzenethiol and 1-butanethiol (Aldrich) were distilled before use. All reactions, except the preparation of **4a** and **4b**, were carried out under nitrogen.

3-(Bromomethyl)-3-methyl-2,3-dihydrobenzofuran (5b). A solution of **4b** (105 mg) in dry Me_2SO (2.0 mL) was added to a solution of dry copper(II) bromide (90 mg) in Me_2SO (2.0 mL). After the mixture had been stirred for 15 h at room temperature, it was diluted with water and extracted 3 times with ether. The combined extracts were washed with water and dried, and the solvent was removed under reduced pressure. The resultant oil was purified by preparative TLC (20% Et_2O /hexane) and distilled to afford **5b** (80 mg, 89%) as an oil: bp 55 °C (block) (0.1 mm); n_{D}^{25} 1.5650; MS (relative intensity), m/z 228 (25%, M^+), 226 (25%, M^+), 147 (30%), 146 (28%), 145 (30%), 133 (100%), 131 (58%); ¹H NMR δ 1.50 (s, 3 H), 3.46 (s, 2 H), 4.09 and 4.53 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 6.6–7.3 (m, 4 H); IR 1611, 1598, 1480, 1211, 1012, 972, 827 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{BrO}$: C, 52.89; H, 4.88. Found: C, 53.33; H, 4.95. This compound was shown to be homogeneous by GLC (column A, 150 °C).

3-(Bromomethyl)-2,3-dihydrobenzofuran (5a). Treatment of **4a** with copper(II) bromide as described above afforded **5a** (82%) as an oil: bp 85 °C (block) (0.7 mm); $n_{\text{D}}^{16.5}$ 1.5834; MS (relative intensity), m/z 214 (9%, M^+), 212 (9%, M^+), 133 (10%), 131 (10%), 121 (100%), 91 (38%); ¹H NMR δ 3.1–4.2 (m, 3 H), 4.2–4.8 (m, 2 H), 6.6–7.4 (m, 4 H); ¹³C NMR δ 35.0 (t), 44.9 (d), 76.0 (t), 110.3 (d), 120.9 (d), 124.7 (d), 127.8 (s), 129.7 (d), 160.6 (s); IR 1610, 1600, 1485, 1240, 975, 850, 760, 655 cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_9\text{BrO}$: C, 50.73; H, 4.26. Found: C, 50.86; H, 4.40.

3-(Chloromethyl)-3-methyl-2,3-dihydrobenzofuran (5c). A solution of **4b** (105 mg) in Me_2SO (2.0 mL) was added to a solution of anhydrous copper(II) chloride (54 mg) in Me_2SO (2.0 mL). The resultant solution was stirred for 15 h at ambient temperature. After this time, the mixture was added to water and extracted 3 times with ether. The combined extracts were washed with water, dried, and concentrated. The oil was subjected to preparative TLC and distilled to afford **5c** (46 mg, 63%) as an oil: bp 50 °C (block) (0.1 mm); n_{D}^{25} 1.5420; MS (relative intensity) m/z 184 (11%, M^+), 182 (32%, M^+), 170 (3%), 168 (9%), 133 (100%), 131 (19%), 105 (55%); ¹H NMR (CCl_4) δ 1.49 (s, 3 H), 3.54 (s, 2 H), 4.09 and 4.55 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 6.6–7.3 (m, 4 H); IR (CCl_4) 1608, 1597, 1476, 1457, 1281, 1215, 1010, 975 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{ClO}$: C, 65.76; H, 6.07. Found: C, 65.94; H, 6.30.

3-(Cyanomethyl)-3-methyl-2,3-dihydrobenzofuran (5d). A solution of **4b** (105 mg) in Me_2SO (2.0 mL) was added to a solution, which had been stirred for 10 min, of copper(I) cyanide (36 mg) in pyridine (2.0 mL). An immediate evolution of gas was observed, and the mixture rapidly darkened. After 10 min, the mixture was diluted with water and 1,2-diaminoethane (ca. 200 mg) was added. The resultant mixture was extracted 4 times with ether. The combined extracts were washed successively with 10% aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and brine. After the solvent had been removed from the dried organic phase, the residue was subjected to preparative TLC and distilled to afford **5d** (28 mg, 40%) as an oil: bp 80 °C (block) (0.15 mm); n_{D}^{25} 1.5344; MS (relative intensity), m/z 173 (34%, M^+), 133 (100%), 131 (13%), 105 (64%), 77 (15%); ¹H NMR δ 1.57 (s, 3 H), 2.60 (s, 2 H), 4.22 and 4.42 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 6.7–7.5 (m, 4 H); IR (CCl_4) 2236, 1610, 1599, 1477, 1560, 1550, 1223, 1208, 1010, 980, 904 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: C, 76.28; H, 6.40. Found: C, 76.27; H, 6.69.

3-Methyl-3-((phenylthio)methyl)-2,3-dihydrobenzofuran (5e). Benzenethiol (44 mg) was added to a suspension of sodium hydride (10 mg) in Me_2SO (2.0 mL), and the mixture was stirred for 5 min. After this period, a solution of **4b** (105 mg) in Me_2SO (2.0 mL) was added. The reaction mixture was stirred for 60 min, then diluted with water, and extracted 3 times with ether. The combined extracts were washed successively with 10% aqueous sodium hydroxide solution and water. The solvent was removed from the dried organic phase, and the residue was subjected to preparative TLC (10% Et_2O /hexane) and distilled to give **5e** (61 mg, 60%) as an oil: bp 100 °C (block) (0.1 mm); n_{D}^{17} 1.6111; MS (relative intensity), m/z 256 (10%, M^+), 133 (100%), 124 (29%), 105 (25%); ¹H NMR (CCl_4) δ 1.43 (s, 3 H), 3.12 (s, 2 H), 4.06 and 4.44 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 6.4–7.4 (m, 9 H); IR 1610, 1599, 1585, 1480, 1460,

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(25) Brokken-Zijp, J.; Bogaert, H. *Tetrahedron* **1973**, *29*, 4169–4174.

(26) Leuckart, R. *J. Prakt. Chem.* **1890**, *41*, 179–224.

1220, 980, 755, 695 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$: C, 74.98; H, 6.29. Found: C, 74.95; H, 6.29.

3-((Phenylthio)methyl)-2,3-dihydrobenzofuran (5g). Benzenethiol (132 mg) and copper powder (170 mg) were added to a stirred mixture of sodium hydride (30 mg) in dry Me_2SO (6.0 mL) at room temperature. After 15 min, when the evolution of hydrogen had ceased, a solution of **4a** (298 mg) in Me_2SO (6.0 mL) was added. The mixture was stirred vigorously for 30 min, by which time the evolution of nitrogen had subsided. The mixture was then diluted with water and extracted 3 times with ether. After the combined extracts had been washed successively with water, 10% aqueous sodium hydroxide solution, and water, they were dried and concentrated. The concentrate was subjected to flash chromatography (15% CH_2Cl_2 /petroleum ether) to afford **5g** (155 mg, 53%) as an oil: bp 105 $^\circ\text{C}$ (block) (0.1 mm); n_{D}^{20} 1.6214; MS (relative intensity), m/z 242 (19%, M^+), 124 (44%), 119 (100%), 91 (55%), 77 (24%); $^1\text{H NMR}$ δ 2.7-3.3 (m, 2 H), 3.3-3.8 (m, 1 H), 4.1-4.8 (m, 2 H), 6.6-7.4 (m, 9 H); $^{13}\text{C NMR}$ δ 39.0 (t), 41.7 (d) 76.2 (t), 110.0 (d), 120.7 (d), 124.7 (d), 126.7 (d) 129.1 (d), 129.3 (d), 130.1 (d), 135.8 (s), 160.3 (s); IR 1595, 1585, 1480, 1460, 1230, 965, 750, 695 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.36; H, 5.82. Found: C, 74.09; H, 5.91. A similar experiment, carried out without the copper powder, gave identical results.

3-((Butylthio)methyl)-3-methyl-2,3-dihydrobenzofuran (5h). 1-Butanethiol (36 mg) was added to a stirred suspension of sodium hydride (10 mg) in Me_2SO (2.0 mL). After 15 min, a solution of **4b** (105 mg) in Me_2SO (2.0 mL) was added, and the resultant mixture was stirred for a further 10 min. The mixture was worked up as in the previous experiment and was subjected to flash chromatography to give **5h** (39 mg, 41%) as an oil: bp 110 $^\circ\text{C}$ (block) (0.1 mm); n_{D}^{15} 1.5422; MS (relative intensity), m/z 236 (4%, M^+), 134 (14%), 133 (100%), 132 (36%), 105 (57%); $^1\text{H NMR}$ δ 0.7-1.9 (m, 7 H), 2.40 (t, $J = 7$ Hz, 2 H), 2.70 (s, 2 H), 4.06 and 4.43 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 6.5-7.3 (m, 4 H); IR 1610, 1600, 1485, 1460, 1215, 1020, 980, 840, 760 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{OS}$: C, 71.16; H, 8.53. Found: C, 71.13; H, 8.28.

An experiment identical with the one above, except that copper powder was present (as described in the preparation of **5g**), afforded **5h** in 64% yield. The spectral data and refractive index were identical with those of the sample prepared above.

S-((3-Methyl-2,3-dihydrobenzofuran-3-yl)methyl) O-Ethyl Dithio-

carbonate (5i). A solution of **4b** (315 mg) in acetone (6.0 mL) was added to a stirred solution of potassium *O*-ethyl dithiocarbonate (240 mg) in acetone (6.0 mL). The evolution of nitrogen was instantaneous. The mixture was stirred for 10 min at room temperature and then was boiled for 3 min under reflux. After the solvent had been removed under reduced pressure from the cooled mixture, ether and water were shaken with the residue. The organic phase was separated and dried. The solvent was then removed, and the resultant oil was subjected to flash chromatography (30% CH_2Cl_2 /petroleum ether) to give **5i** (242 mg, 75%) as an oil: n_{D}^{26} 1.5905; MS (relative intensity), m/z 268 (6%, M^+), 133 (100%), 105 (46%), 91 (13%), 77 (9%); $^1\text{H NMR}$ δ 1.35 (t, $J = 7$ Hz, 3 H), 1.43 (s, 3 H), 3.46 (s, 2 H), 4.11 and 4.39 (AB q, $J_{\text{AB}} = 9$ Hz, 2 H), 4.53 (q, $J = 7$ Hz, 2 H), 6.5-7.2 (m, 4 H); $^{13}\text{C NMR}$ δ 13.7 (q), 24.5 (q), 45.7 (t), 46.0 (s), 70.3 (t), 81.7 (t), 110.2 (d), 120.9 (d), 123.2 (d), 129.1 (d), 133.4 (s), 160.6 (s), 177.2 (s); IR 1610, 1595, 1480, 1455, 1220, 1110, 1050, 980, 755 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}_2$: C, 58.20; H, 6.01. Found: C, 58.07; H, 5.58.

(3-Methyl-2,3-dihydrobenzofuran-3-yl)methanethiol (5j). A solution of **5i** (220 mg) in 1,2-diaminomethane (1.5 mL) was stirred under nitrogen overnight at ambient temperature. The mixture was then poured into water and extracted 3 times with ether. After the combined ether extracts had been washed successively with 10% aqueous hydrochloric acid and water, they were dried and concentrated. The resultant oil was purified by flash chromatography (80% CH_2Cl_2 /petroleum ether) to afford **5j** as an oil (144 mg, 77%). Although this compound was homogeneous on GLC (column B, 125 $^\circ\text{C}$), $^1\text{H NMR}$ examination indicated that an unidentified minor impurity was present (<20%). Further purification was inefficient, but distillation of a portion, afforded a small analytical sample: bp 110 $^\circ\text{C}$ (block) (0.5 mm); MS (relative intensity), m/z 180 (4%, M^+), 133 (61%), 105 (100%), 79 (20%), 77 (30%); $^1\text{H NMR}$ δ 1.23 (t, $J = 9$ Hz, 1 H), 1.43 (s, 3 H), 2.73 (d, $J = 9$ Hz, 2 H), 4.14 and 4.51 (AB q, $J_{\text{AB}} = 9$ Hz, 2H), 6.6-7.3 (m, 4 H); IR 2570, 1610, 1600, 1480, 1450, 1225, 1000, 985, 840, 755 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{OS}$: C, 66.65; H, 6.71. Found: C, 66.65; H, 6.67.

Registry No. **4a**, 25125-40-0; **4b**, 56182-25-3; **5a**, 78739-85-2; **5b**, 78739-86-3; **5c**, 78739-87-4; **5d**, 78739-88-5; **5e**, 78739-90-9; **5g**, 103304-48-9; **5h**, 78739-89-6; **5i**, 103304-49-0; **5j**, 103304-50-3; BuSH, 109-79-5; EtOC(S)SK, 140-89-6; $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, 107-15-3.

Formation of Some Bi- and Tricyclic Systems by Radical Ring Closure¹

Athelstan L. J. Beckwith* and David H. Roberts[†]

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. Received March 6, 1986

Abstract: Reductive alkylation of methyl benzoate with 1,3-dibromopropane affords a (bromopropyl)cyclohexadiene **3a** treatment of which with tributylstannane gives the hydroindane derivative **4a** via ring closure of the radical **25**. Similar reactions of suitable substituted dienes (e.g., **3b,c**), dienones (e.g., **23**), and related compounds (e.g., **14**) with tributylstannane or tributylgermane give mixtures of cyclized products the relative amounts of which allow the effects of substituents on the rate of cyclization to be determined. The results show that vinylic substituents at the seat of attack (α -substituents) strongly retard addition, that the β -methyl substituent in **6b** is weakly activating, that the β -methoxy substituents in **6** and **12** have a negligible effect, and that dienone radicals (e.g., **31**) are much more reactive than the corresponding diene radicals (e.g., **25**). The rate constants, k_c , for ring closure and activation parameters were determined by comparison with k_H the rate constant for reaction of alkyl radicals with tributylstannane. Captodative stabilization of the product radical **43** has only a small rate-enhancing effect on cyclization of the radical **32**, containing both methoxy and carbonyl groups.

Numerous recent examples^{2,3} have illustrated the increasing importance of free radical methods in synthetic chemistry. Ring formation by intramolecular homolytic addition³⁻⁵ has attracted particular interest since it can often be carried out efficiently under

mild conditions and with such chemoselectivity that the use of protecting groups is minimized. Furthermore, cyclization fre-

[†] Present address: Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

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