$CO_2CH_2CH_3$, 14%) were produced, together with a good deal of polymer.[5] Interestingly, polymer formation was eliminated in benzene–methanol–acetic acid solution (equal volumes of each solvent component);[1] formation of 8 (29%) and 9 (35%) and extensive ether cleavage (35%) was noted. Formation of *cis*-fused decalone 8 (67% yield), with no evidence for formation of 9 or 4 ($R = CO_2CH_2CH_3$), occurred when irradiation (366 nm) of **1b** was performed in benzene solution in the presence of the triplet sensitizer benzophenone.

Assignment of stereochemistry in **3**, **6**, and **9** is based on NMR spectral data and chemical reactivity. Thus, in the NMR spectra of **3**, **6**, and **9**, H_a appears as a sharp singlet at 4.43, 4.50, and 4.43 ppm, respectively. In that for **8**, H_a appears at 5.10 ppm and experiences W coupling ($J_{ab} = 1.5$ Hz). While **8** and **9** are not thermally interconvertible below 140 °C (refluxing xylene solution), **8** undergoes transformation into **9** in refluxing benzene solution saturated with *p*-toluenesulfonic acid (half-life ~5 h) or refluxing benzene–acetic acid solution (equal volumes of each solvent component, half-life ~14 h). Treatment of either **8** or **9** with 1 N potassium hydroxide in methanol followed by acidification gave a single lactol **10** (mp 232–233 °C).[5] NMR absorption for H_a in **10** appears as a sharp singlet at 4.25 ppm. Finally, **8** and **9** give lactone **11** (ir 5.69 and 5.80 μ) on treatment with zinc dust in refluxing propionic acid solution.[1]

In contrast to conversions **1** → **7a**, in which ring B may assume a chair conformation, conrotatory photocyclization of **2**, to give a cis-AB ring fusion, must result in a carbonyl ylide possessing a ring-B boat conformation. On the other hand, cyclization of **2**, to give a trans-AB ring fusion, would maintain the ring-B chair conformation present in **2**.[6] A carbonyl ylide derived from **2**, with a trans-AB ring fusion, would be expected to have approximately the same ring strain as hypothetical **7b**, while a carbonyl ylide with a cis-AB ring fusion should be somewhat more strained than **7a**. If the additional ring strain imposed on **7a** is significant, then photocyclization of **2** might be expected to be less stereoselective than that of **1a**. In fact, photolysis of **2** did not produce a dihydrofuran with a trans-AB ring fusion, but rather gave cis-fused **6** in high yield along with a small amount of ether cleavage.

Thus, our studies with **1b** indicate that, while replacement of the methyl group in **1a** with the bulky carbethoxy group does seem to make photocyclization less facile (note extensive ether cleavage in **1b**), this steric alteration does not lead to a detectable inversion in stereoselectivity of carbonyl ylide formation. Furthermore, the constraints imposed by the steroid framework in **2**, which would seem to operate in discord with formation of a cis-AB ring fusion, also do not alter stereoselectivity of carbonyl ylide formation. In general then, photocyclization–rearrangement of 1-aryloxy-$\Delta^{1(9)}$-octalone-2 systems should produce a dihydrofuran possessing a *cis*-decalone ring fusion. Application of the principles discussed here to the synthesis of complex organic molecules along with a detailed investigation of excited singlet and triplet state reactivity in aryloxyenones is currently being investigated.

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References and Notes

(1) A. G. Schultz and R. D. Lucci, *J. Org. Chem.*, **40**, 1371 (1975).

(2) Aryloxyenones **1a** (mp 71–73 °C) and **2** (mp 122–123 °C) were prepared from phenol and the corresponding epoxy ketone by a method previously reported,[1] while preparation of **1b** (mp 62–64 °C) followed an annelation approach from ethyl 2-cyclohexanonecarboxylate and 1-phenoxy-3-buten-2-one, the details of which will be described elsewhere.

(3) The methodological term heteroatom directed photoarylation is intended to characterize photochemically initiated electrocyclic reactions, which, by influence of an appropriate heteroatom, result in bond formation between two atoms at least one of which initially resides in an aromatic nucleus. In the present case, formation of a *carbon-carbon* bond is "directed" by an oxygen atom to give a dihydrobenzofuran. It should be noted that a variety of previously studied photoreactions may be considered to belong to this general reaction classification. To cite a few, the elegant investigation of "non-oxidative photocyclization" of *N*-aryl enamines [O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, *J. Am. Chem. Soc.*, **93**, 2918 (1971)] and the photocyclization of benzoic acid anilides [B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 615 (1967)], acrylic acid anilides [P. G. Cleveland and O. L. Chapman, *ibid.*, 1064 (1967)], and biaryl isocyanates [J. S. Swenton, T. J. Ikeler, and G. LeRoy Smyser, *J. Org. Chem.*, **38**, 1157 (1973)] are well-known examples.

(4) A. G. Schultz and M. B. DeTar, *J. Am. Chem. Soc.*, **96**, 296 (1974).

(5) The acid- or base-catalyzed conversion of **8** to **9** must occur as a result of enolization at the carbon bearing H_a. We assume that tautomerization will occur to give the stable *cis*-dihydrofuran ring fusion in **9** as shown; see ref 1. Remaining stereochemical assignment in **8** must await further structural studies.

(6) Crystallographic studies with progesterone [H. Campsteyn, L. Dupont, and O. Dideberg, *Acta Crystallogr.*, **B28**, 3032 (1972)], testosterone [G. Precigouz et al., *Cryst. Struct. Commun.*, **2**, 435 (1973)], and 26-hydroxycholestenone *p*-bromobenzoate [E. Caspi et al., *J. Am. Chem. Soc.*, **93**, 6283 (1974)] demonstrate that ring B in all of these compounds assumes a chair conformation.

(7) Postdoctoral research associate 1973–1975.

Arthur G. Schultz,* Wallace Y. Fu[7]
Department of Chemistry, Cornell University
Ithaca, New York 14853

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1,4,5,8-Tetrathiatetralin, a Tetrathiafulvalene Isomer

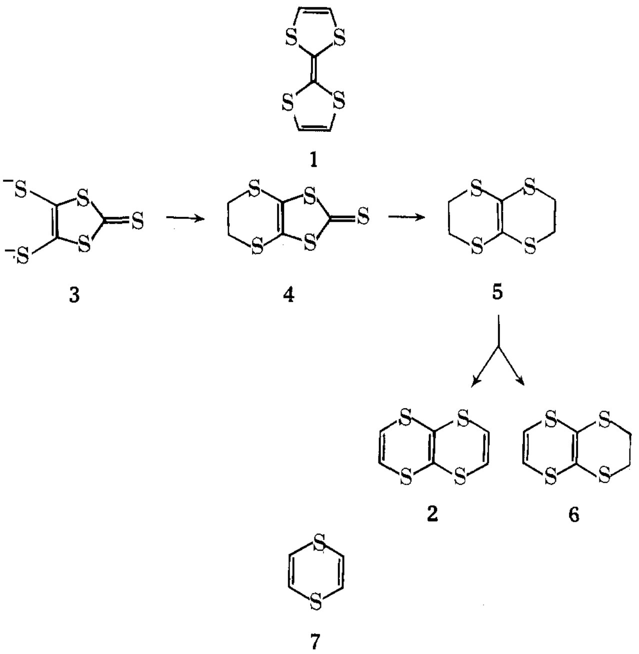
Summary: 1,4,5,8-Tetrathiatetralin (**2**) has been obtained by a four-step synthesis from carbon disulfide. Compound **2**, unlike the isomeric tetrathiafulvalene (**1**), is not readily oxidized to a cation radical.

Sir: Tetrathiafulvalene (**1**) and its selenium analogs have been the subject of great interest, since they are valuable π donors in the preparation of charge-transfer salts having metallic properties.[1] The hitherto unknown 1,4,5,8-tetrathiatetralin (**2**)[2] is an isomer of **1** which differs structurally from the latter only in the arrangement of the two ethyne bridges. We now report the first synthesis of **2** and some physical and electrochemical properties of this substance.

Electrochemical reduction of carbon disulfide to the dianion **3**,[3] followed by alkylation with 1,2-dibromoethane, gave (18%) trithiocarbonate **4** as golden plates, mp 121.5–122.5 °C. Hydrolysis of **4** by hot ethanolic potassium hydroxide, followed by alkylation with 1,2-dibromoethane, gave (70%) the tetrahydro derivative **5** of **2** as white needles, mp 154–156 °C. Compound **5** was dehydrogenated by refluxing overnight with DDQ in xylene to give, after silica chromatography, the dihydro derivative **6** of **2** (45%) as pale yellow needles, mp 80–81 °C, as well as **2** itself (37%) in the form of lemon yellow needles: mp 125–126 °C; $\lambda_{max}^{cyclohexane}$ 235 nm (ϵ 8000), 248 (sh, 6100), 270 (sh, 5000).

Although **2** may be viewed as a potentially aromatic 14-π-electron system, its NMR spectrum ($CDCl_3$) shows a singlet at δ 6.46 ppm, a position very close to that (6.55) of the olefinic protons of its dihydro derivative **6**. This observation suggests that **2**, like the parent monocyclic analog *p*-dithiin,[4] lacks aromatic stabilization and thus, may possess a nonplanar conformation.

Moreover, in sharp contrast to **1**, **2** is not readily oxidized by tetracyanoquinodimethane to give a radical ion charge-transfer salt. A quantitative measure of this difference in



oxidative behavior is directly provided by polarographic measurements. Whereas **1** is reversibly oxidized with values of 0.006 V and 0.385 V for $E_{1/2}{}^1$ and $E_{1/2}{}^2$, **2** is oxidized with corresponding values of 0.561 V and 0.965 V, where the second oxidation step occurs irreversibly.[5] This lack of relative ease to oxidize **2** hinders its use as a donor cation in highly conducting organic metals.

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References and Notes

(1) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
(2) The more cumbersome systematic name of **2** is 1,4-dithiino[2,3-*b*]-1,4-dithiin. Satisfactory elemental analyses were obtained for compounds **2**, **4**, **5**, and **6**.
(3) S. Wawzonek and S. M. Heilmann, *J. Org. Chem.*, **39**, 511 (1974).
(4) W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. M. Curtis, and W. L. Lipscomb, *J. Am. Chem. Soc.*, **76**, 4957 (1954).
(5) Measured in CH_3CN with tetraethylammonium perchlorate (0.05 M) added vs. Ag/Ag^+ (0.1 N in CH_3CN) with a glassy carbon electrode (GCE) as the working electrode.
(6) (a) Department of Chemistry; (b) Department of Physics.

Masao Mizuno,[6a] Michael P. Cava,*[6a]
Anthony F. Garito[6b]
Departments of Chemistry and Physics and
Laboratory for Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19174

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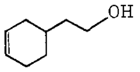
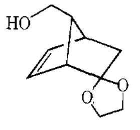
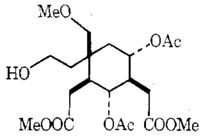
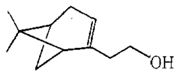
Organoselenium Chemistry. A Facile One-Step Synthesis of Alkyl Aryl Selenides from Alcohols

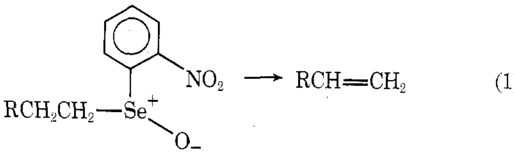
Summary: Treatment of alcohols with aryl selenocyanates in either tetrahydrofuran or pyridine containing tributylphosphine results in high yields of alkyl aryl selenides.

Sir: Substituents on the β and/or γ carbons of primary alkyl phenyl selenoxides result in low yields of terminal olefins. Recently it was demonstrated[1,2] that primary alkyl *o*-nitrophenyl selenoxides undergo facile elimination with formation of terminal olefins in high yield (eq 1). For example, the *o*-nitrophenyl selenoxide derived from cyclohexylmethanol provides a twofold increase in the yield of *exo*-methylenecyclohexane as compared to the corresponding phenyl selenoxide.[1] *o*-Nitrophenyl selenoxides are generated by oxidation of the corresponding alkyl *o*-nitrophenyl selenides which are prepared by displacement of alkyl tosylates, mesylates, or halides with the corresponding selenium anion (eq 2). The *o*-nitrophenyl selenium anion is generated by treatment of *o*-nitrophenyl selenocyanate with sodium borohydride in either absolute ethanol[1] or dimethylformamide[2b] (eq 2). We wish to describe in this communication the direct one-step conversion of alcohols to alkyl aryl selenides (eq 3).

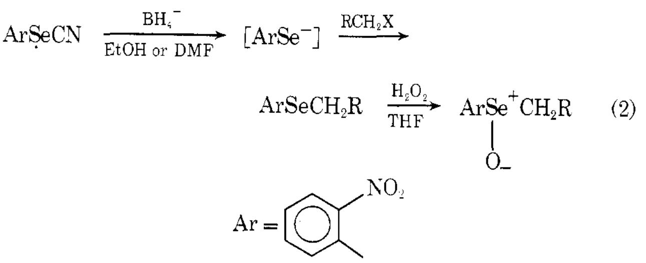
Table I. Conversion of Alcohols to Alkyl *o*-Nitrophenyl Selenides

Compound	% yield of selenide[a–c] in pyridine	% yield of selenide[a–c] in THF
1-Dodecanol	92	94
1-Heptanol	85	
3-Hexyn-1-ol	93	88
Benzyl alcohol	97	93
Cyclohexylmethanol	99	88
	98	95
	91	90
		91
	98	85
2-Propanol	93	
Cyclooctanol		63

[a] All compounds were fully characterized by spectral methods. [b] Yields reported are for isolated, chromatographically pure substances. [c] All reactions were performed at room temperature in the presence of the indicated solvent.



$$\mathrm{RCH_2CH_2{-}\overset{+}{Se}(O^-){-}C_6H_4NO_2} \longrightarrow \mathrm{RCH{=}CH_2} \qquad (1)$$



$$\mathrm{ArSeCN} \xrightarrow[\text{EtOH or DMF}]{\mathrm{BH_4^-}} [\mathrm{ArSe^-}] \xrightarrow{\mathrm{RCH_2X}} \mathrm{ArSeCH_2R} \xrightarrow[\mathrm{THF}]{\mathrm{H_2O_2}} \mathrm{Ar\overset{+}{Se}(O^-)CH_2R} \qquad (2)$$

Ar = *o*-nitrophenyl

$$\mathrm{RCH_2OH} \xrightarrow[\text{THF or pyridine}]{\mathrm{ArSeCN/Bu_3P}} \mathrm{RCH_2SeAr} \qquad (3)$$

Treatment of a variety of primary alcohols with *o*-nitrophenyl selenocyanate[3] in tetrahydrofuran or pyridine at room