One-step Synthesis of Methoxycarbonyl-substituted Tetraselenafulvalene under High Pressure

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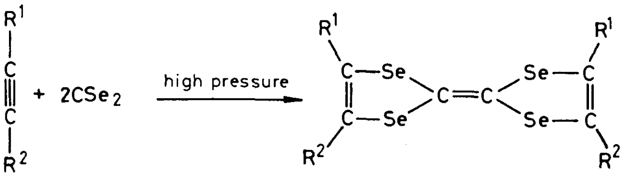
Summary The reactions of methyl propiolate and dimethyl acetylenedicarboxylate with CSe_2 in dichloromethane at 60—65 °C under 4500—5000 atm for 10 h gave dimethoxycarbonyl- and tetramethoxycarbonyl-substituted tetraselenafulvalenes in good yield (*ca.* 85—90%).

Since the discovery that tetrathiofulvalene (TTF) can form a charge-transfer complex with tetracyanoquinodimethane (TCNQ), which has unusually high electrical conductivity, there has been much interest in the synthesis and characterization of TTF and its complexes.[1,2]

In the search for charge-transfer complexes of superior conductivity the synthesis of TTF analogues in which some or all of the sulphur atoms have been replaced by the more polarizable chalcogen selenium atoms, such as tetraselenafulvalene (TSeF) and its derivatives, have been studied.[3–6]

One of the simplest routes reported for the synthesis of TSeF involved the starting reagent carbon diselenide (CSe_2) and proceeded *via* the synthesis of 1,3-diselenolane-2-selone.[4]

It is well known that liquid-phase reactions characterized by multiple bond formation are generally facilitated by the application of hydrostatic pressure.[7] Recently, an elegant organic synthesis under high pressure, namely the synthesis of cantharidin, was reported by Dauben, Kessel, and Takemura.[8] We have shown that certain tetrathiofulvalene derivatives can be readily synthesized by the reaction of the corresponding acetylenic compounds with CS_2 under high pressure in the absence of catalyst.[9] We now report a simple one-step synthesis of methoxycarbonyl-substituted tetraselenafulvalenes from which TSeF can be readily obtained by heating with LiBr.[4]



(1) (2) *cis* and *trans*

a ; $R^1 = CO_2Me$, $R^2 = H$
b ; $R^1 = R^2 = CO_2Me$

The reactions of methyl propiolate and dimethyl acetylenedicarboxylate with CSe_2 in dichloromethane at 60—65 °C under 4500—5000 atm for 10 h gave dimethoxycarbonyl- and tetramethoxycarbonyl-substituted TSeF in good yields (*ca.* 85—90%).† Carbon diselenide was found to be more reactive toward the acetylenic compounds than carbon disulphide. However, without the application of pressure to the reaction systems, the reactions were found to be very slow or not to proceed. Typical experimental results are summarized in the Table.

TABLE. Reactions of methoxycarbonyl-substituted acetylenes with CSe_2 under pressure.

Reactant	T/°C	t/h	Pressure/atm	Product (yield/%)
(**1b**)	60	13	5000	(**2b**) (90)[a]
(**1b**)	70—80	72	in sealed tube	(**2b**) (10)[a]
(**1a**)	60	13	5000	(**2b**) (85)[b]
(**1a**)	70—80	72	in sealed tube	0

[a] Tetramethoxycarbonyltetraselenafulvalene, m.p. 144—145 °C (lit.,[4] 144—145 °C); ν (KBr) 1720, 1565, 1435, 1250, and 1275 cm^{-1}; λ_{max} (cyclohexane) (log ε) 260 (4·40), 285 (4·43), 328sh (3·70), and 422 nm (3·56); m/e 628 (based on ^{80}Se); δ 3·83 (s). Under these conditions it was found that CSe_2 did not polymerize and was recovered quantitatively. [b] Dimethoxycarbonyltetraselenafulvalene, m.p. 161—162 °C; ν(KBr) 1710, 1535, 1430, and 1240 cm^{-1}; λ_{max} (cyclohexane) (log ε) 249 (4·34), 254 (4·44), 261 (4·44), 283 (4·25), 326 (3·90), and 420 nm (3·47); m/e 512 (based on ^{80}Se); δ 3·75 (s).

This work also represents one more example of the usefulness of high-pressure technology for the synthesis of relatively complex organic compounds.

We are grateful to the Koppers Company, Inc., for support of this work with a generous grant.

(*Received*, 18*th March* 1981; *Com.* 306.)

† A typical reaction procedure under high pressure is as follows. A mixture of dimethyl acetylenedicarboxylate (0·28 g) and CSe_2 (0·34 g) in CH_2Cl_2 (3 ml) was heated under an hydraulic press (for the high-pressure reaction procedure, see Y. Okamoto and H. Shimizu, *J. Am. Chem. Soc.*, 1968, **90**, 6145). Pressure was controlled within ±300 atm. A dark solid and red solution were obtained. The odour of CSe_2 (rotten radish) disappeared on completion of the reaction. After the solvent was removed *in vacuo*, the solid was washed with benzene. The dried solid (0·58 g) had m.p. 136—142 °C, yield 93%. The crude product was recrystallized from methanol–benzene, m.p. 144–145 °C (lit.,[4] 144—145 °C). CSe_2 was synthesized according to the literature (D. J. G. Ives, R. W. Pittman, and W. Wardlaw, *J. Chem. Soc.*, 1947, 1080) and was also obtained from Alfa products.

[1] J. Ferraris, D. D. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.
[2] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, 1973, **12**, 1125.
[3] E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, 1974, **96**, 7376.
[4] M. V. Lakshmikanthan and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 882.
[5] M. V. Lakshmikanthan and M. P. Cava, *J. Org. Chem.*, 1980, **45**, 2632.
[6] M. Narita and C. U. Pittman, Jr., *Synthesis*, 1976, **8**, 489.
[7] K. E. Weale, 'Chemical Reactions at High Pressure,' E. and F. N. Spon, Ltd., London, 1967, pp. 175—200.
[8] W. G. Dauben, C. R. Kessel, and K. H. Takemura, *J. Am. Chem. Soc.*, 1980, **102**, 6893.
[9] J. E. Rice and Y. Okamoto, *J. Org. Chem.*, 1981, **46**, 446.