FLUORINE-CONTAINING ALLENES
COMMUNICATION 3. * REACTION OF TETRAKIS(TRIFLUOROMETHYL)ALLENES WITH ETHYL MERCAPTAN

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The free-radical addition of mercaptans and thiophenol to allene and its homologs has been studied in sufficient detail [3]. The direction of attack by the radical particle is strongly dependent on the degree of substitution of the C atoms in the allene system. The ethylthiyl radical attacks mainly the terminal C atoms of allene [4]. Attack of the central C atom of the cumulene system begins to predominate as the H atoms of the CH₃ group are replaced. In unsymmetrical 1,1-dimethylallene the radical particle adds 100% to the central C atom.

It was interesting to ascertain whether the character of the substituent in allene affects its reaction with mercaptans. In tetrakis(trifluoromethyl)allene (I) the cumulene system of bonds, being attached to four electrophilic CF₃ groups, is poor in electrons. Consequently, it could be assumed that the reaction of this allene with thyl radicals, which have electrophilic properties [5], will be difficult. Actually, the addition of ethyl mercaptan and thiophenol to (I) is realized at 140-160°C,† in which connection, the same as in the case of allene homologs, the central C atom is attacked exclusively. The obtained 2,4-bis(trifluoromethyl)-3-ethylthio-1,1,1,5,5,5-hexafluoro-2-pentene (II) and 2,4-bis(trifluoromethyl)-3-phenylthio-1,1,1,5,5,5-hexafluoro-2-pentene (III) differ from the unfluorinated analogs by a lower reactivity. They do not add a second molecule of the reactants at the multiple bond, like the simpler alkylallenes [6, 7].

The reaction of (I) with thiophenol proceeds unambiguously, while the reaction with ethyl mercaptan gives a complex mixture of products. Here, besides thioether (II), are formed 2,4-bis(trifluoromethyl)-5,5,5-hexafluoro-2-pentene (IV), diethyl disulfide (V), and 1-ethylthio-2,2,4-tris(trifluoromethyl)-3,3-difluoro-1-cyclobutene (VI). The formation of (IV) and (V) formally represents the hydrogenation of the starting (I) by the ethyl mercaptan. A similar "hydrogenation" of the double bonds occurs when thiophenol is reacted with unsaturated sulfides [8]. The formation of (IV) was also observed in the reaction of (I) with H₂S [9].

The cyclic sulfide (VI) can be regarded to be the result of the thermal elimination of HF from thioether (II). It proved that it easily loses HF when treated with Et₃N. However, the unsaturated compound

*See [1, 2] for Communications 1 and 2.
†The addition of thiophenol to 1,1-dimethylallene is exothermic [4].
cannot be obtained here, apparently due to the reversibility of the reaction. To shift the equilibrium to the right and bind the obtained Et₃N·HF it is necessary to add benzoyl chloride to the reaction mixture (cf. [4] and [10]), in which connection 2,4-bis(trifluoromethyl)-3-ethylthio-1,1,1,5,5-pentafluoro-2,4-diene (VII) was obtained in good yield. Diene (VII) is unstable and easily (even when distilled at atmospheric pressure) undergoes intramolecular cyclization to (VI).

**EXPERIMENTAL**

The 1H NMR spectra were recorded on a Perkin–Elmer R-12 spectrometer using TMS as the external standard; the 19F NMR spectra were taken on a Hitachi H-6013 spectrometer (56.46 MHz) using CF₃COOH as the external standard; the IR spectra were taken on a UR-10 spectrometer. For the analytical and preparative GLC we used Perkin–Elmer 462, Carlo Erba (4 m × 25 mm column packed with 25% QF-1 deposited on Chromosorb), and Varian (2 m × 8 mm column packed with 25% dinonyl phthalate deposited on Chromatone) instruments.

**Reaction of Thiophenol with Tetrakis(trifluoromethyl)allenene (I).** A mixture of 2.3 g (0.007 mole) of allenene (I) and 1.61 g (0.041 mole) of thiophenol was heated in a Carius tube for 30 h at 140°C. The mixture remained heterogeneous. The lower layer was separated from the excess thiophenol and distilled. We obtained 2.8 g (81%) of 2,4-bis(trifluoromethyl)-3-phenylthio-1,1,1,5,5,5-hexafluoro-2-pentene (III) with bp 100-102°C (10 mm). Infrared spectrum: 1580 cm⁻¹ (C=C). Found: C 37.1; H 1.40; F 54.8; S 7.64%. C₁₃H₁₆F₁₂S. Calculated: C 37.0; H 1.42; F 54.1; S 7.60%. 1H NMR spectrum: 4.6 (CH) 7.05 m (phenyl), J₃H--F -- 7.3 Hz. 19F NMR spectrum: --15.0 d [(CF₃)₂CH]; --16.5q (CF₃C=); --22.3 q (CF₃C=); JCF₃/CF₃C = 9.7 Hz.

**Reaction of Ethyl Mercaptan with Tetrakis(trifluoromethyl)allenene (I).** A mixture of 24.8 g (0.0795 mole) of allenene (I) and 7.4 g (0.119 mole) of ethyl mercaptan was heated in a 50 ml steel autoclave for 40 h at 140°C, and then the mixture was distilled. We obtained 7.5 g of a fraction with bp up to 70°C, and 23 g of a fraction with bp 120-150°C. The low-boiling fraction contains the starting mercaptan and the known [9] dihydropentene (IV) (9.3% yield), which was identified by comparing the GLC parameters and the 1H NMR, 19F NMR, and IR spectral data with those of an authentic specimen.

**Reaction of 2,4-Bis(trifluoromethyl)-3-ethylthio-1,1,1,5,5,5-hexafluoro-2-pentene (II) with Triethylamine in the Presence of Benzoyl Chloride.** A mixture of 13.8 g (0.037 mole) of thioether (II), 3.74 g (0.037 mole) of absolute Et₃N, and 5.2 g (0.037 mole) of C₆H₄COCl was heated in a Carius tube for 12 h at 90°C. Then the reaction mixture (16.6 g) was washed 10 times with hot water, and the residual 11.6 g of oil was dried over MgSO₄ and distilled. We obtained 9 g (62.5%) of 2,4-bis(trifluoromethyl)-3-ethylthio-1,1,1,5,5-pentafluoro-2,4-diene (VII) with bp 39°C (10 mm), n₁₀ 1.3735. Infrared spectrum: 1590, 1740 cm⁻¹ (C=C). Found: C 30.6; H 1.48; F 58.1; S 9.02%. C₈H₈F₁₄S. Calculated: C 30.5; H 1.41; F 59.0; S 9.04%. 19F NMR spectrum: --5 m (CF₂=), --17.8 t (CF₃C=), --19 s [(CF₃)₂C]; JCF₃/CF₂ = 11.25 Hz.