Bis(trifluoromethyl)thioketen

By MAYNARD S. RAASCH

(*Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware* 19898)

WE report the synthesis of bis(trifluoromethyl)-thioketen, a reactive compound stable enough to distil, handle, and store without special precautions.

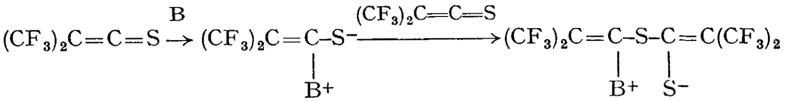
The synthesis of thioketen itself by the pyrolysis of t-butyl ethynyl sulphide was reported by Howard.[1] Thioketen could be collected without solvent at −196° but polymerized on warming to

−80°. When collected in cyclohexene at −80°, it was stable for several hours at that temperature.

With the thought that strongly electron-attracting groups might stabilize the thioketen system, bis(trifluoromethyl)thioketen has now been synthesized by the following sequence. From diethyl sodiomalonate and thiophosgene, tetraethyl 1,3-dithietan-$\Delta^{2,\alpha}$, $\Delta^{4,\alpha}$-dimalonate (I), m.p. 180—181°, was prepared in 70% yield. This is an old compound but had been assigned a different structure.[2] Treatment of the tetra-ester with sulphur tetrafluoride in the presence of hydrogen fluoride[3] in two steps yielded 2,4-bis-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietan* (II), m.p. 85°, b.p. 173°, in 75% yield. Infrared, 6·19 μ; ^{19}F n.m.r. in CCl_4, singlet at −8·4 p.p.m. using $CFCl_2{\cdot}CFCl_2$ as external standard. This dimer was cracked at 650° to give 60—70% of monomeric bis(trifluoromethyl)thioketen* (III), a reddish orange liquid, b.p. 52°, m.p. −54°, n_D^{25} 1·3495, d_4^{25} 1·462, dipole moment 1·96 D. Spectral absorptions: 5·61 μ, 502 mμ (ϵ 8·5), 240 mμ (ϵ 5590), shoulder at 265 mμ (ϵ 600). ^{19}F n.m.r. (neat), singlet at −9·1 p.p.m. using $CFCl_2{\cdot}CFCl_2$ an external standard.

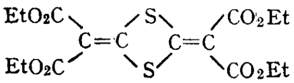
The thioketen dimer (II) can also be made in 60% yield by the reaction of bis(trifluoromethyl)keten[4] with triphenylphosphine sulphide at 200°. Further, the decomposition of 2-diazo-1,1,1,3,3,3-hexafluoropropane[5] or 3,3-bis(trifluoromethyl)-3*H*-diazirine[6] in carbon disulphide produces the cyclic polysulphides, 3,6-bis-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-*s*-tetrathian (IV), m.p. 44·5°, and 3,5-bis-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,2,4-trithiolan (V), b.p. 93°/15 mm. These compounds are converted into the thioketen dimer with triphenylphosphine. A similar reaction with carbon disulphide has been reported for diazodiphenylmethane.[7]

Bis(trifluoromethyl)thioketen may be kept in glass bottles at room temperature for many months with little dimerization. However, the compound is readily dimerized to (II) by Lewis bases such as tertiary amines and various nitrogen-, oxygen-, and sulphur-containing molecules. Presumably, this occurs through a conventional mechanism:

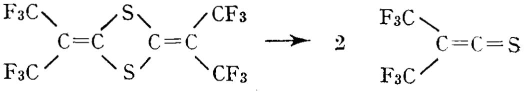


$$(CF_3)_2C{=}C{=}S \xrightarrow{B} (CF_3)_2C{=}\underset{B^+}{\underset{|}{C}}{-}S^- \xrightarrow{(CF_3)_2C{=}C{=}S} (CF_3)_2C{=}\underset{B^+}{\underset{|}{C}}{-}S{-}\underset{S^-}{\underset{|}{C}}{=}C(CF_3)_2$$

Loss of B results in dimer if the catalysis is carried out above about −20°. At lower temperatures, polymer formation sets in. The thioketen is polymerized by adding it to acetone at −80°. The polymer* is white, insoluble in all solvents tried, and melts at 245° with cracking back to the monomer. Infrared shows C=C absorption at 6·35 μ.

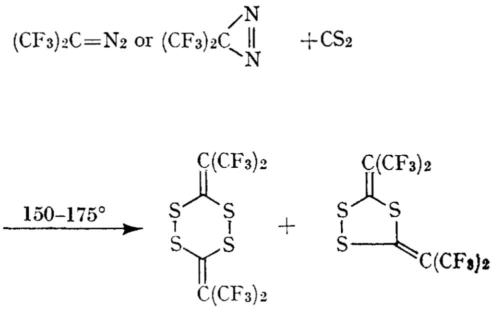


(I)



(II) (III)

Fortunately, the dimerization is not as rapid as many of the reactions of the thioketen. The thioketen forms thioamides from primary and secondary amines, *e.g.*, 4′-chloro-3,3,3-trifluoro-2-(trifluoromethyl)thiopropionanilide,* p-ClC_6H_4-$NHCS{\cdot}CH(CF_3)_2$, m.p. 54·5–55°, from p-chloroaniline. Proton n.m.r. in CCl_4, septuplet centred at 4·69 p.p.m. for $(CF_3)_2CH$ and singlet at 8·71 p.p.m. for NH. Cyclizations generally involve addition to the thiocarbonyl group. Thus, Diels–



(IV) (V)

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* Satisfactory elemental analyses were obtained for new compounds indicated thus.

Alder addition with 2,3-dimethylbutadiene yields 3,6-dihydro-4,5-dimethyl-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-2*H*-thiopyran,* b.p. 96—98°/9 mm., n_D^{25} 1·4503. The proton n.m.r. spectrum (neat) shows only a sharp peak at 1·67 p.p.m. for CH_3 and a broadened peak at 3·05 p.p.m. for CH_2. The ^{19}F spectrum consists of two quadruplets.

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