Carbon Monoxide Reactions: a Novel Synthesis of Chlorothiolformates

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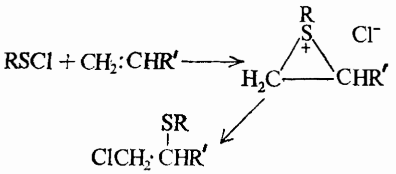
FREE-RADICAL additions to carbon monoxide wherein chlorocarbonyl groups are formed ("chlorocarbonylation") have been the subject of previous investigations in this series.[1] We now report that chlorothiolformates, another class of compounds containing the COCl linkage, can be synthesized from the addition of sulphenyl chlorides to carbon monoxide.

$$\mathrm{RSCl + CO \rightarrow RSCOCl}$$

Simple alkyl- and aryl-sulphenyl chlorides behave as positive-sulphur compounds and readily undergo reactions with unsaturated compounds by what appears to be electrophilic attack and the formation of episulphonium intermediates.[2]



Several sulphenyl chlorides containing electronegative substituents ($\mathrm{Cl_3CSCl}$[3], $\mathrm{F_3CSCl}$[4]) undergo homolytic addition to unsaturated compounds. The fact that carbon monoxide reacts with positively charged species[5] and with free radicals suggested that its reaction with sulphenyl chlorides might provide a new route to chlorothiolformates.

A variety of sulphenyl chlorides was screened to determine the scope of this reaction. The sulphenyl chloride (neat or in $\mathrm{CCl_4}$ solution) was shaken overnight at 25° with carbon monoxide at 6000 lb./in.^{2}. The reaction mixture was analysed by i.r. spectroscopy to determine whether any carbonyl had been incorporated. In some circumstances conversions could be determined quantitatively from the ratio of the n.m.r. signals (*e.g.* MeSCl, 2·92 p.p.m.; $\mathrm{CH_3SCOCl}$, 2·47 p.p.m.).

In the initial screening experiment (6000 lb./in.^{2} CO) methanesulphenyl chloride was completely converted into methyl chlorothiolformate, 90% of which could be isolated by distillation (b.p. 54°/103 mm., n_D^{30} 1·4849). At 1000 lb./in.^{2} CO pressure the reaction was complete in less than 7 hr. and an 89% yield of methyl chlorothiolformate was isolated by distillation. Using 300 lb./in.^{2} CO pressure the reaction showed 60% conversion in 4 hr. at 25° and 50% conversion in 8 hr. at 0°. In all cases the reaction was complete in less than 12 hr.

Benzenesulphenyl chloride reacted under 6000 lb./in.^{2} carbon monoxide pressure at 25° to give a 99% crude yield of a yellow liquid (n_D^{30} 1·5831). A 95% yield of pure phenyl chlorothiolformate (n_D^{30} 1·5787) was isolated by distillation (96—99·5°/12 mm.). The reaction of benzensulphenyl chloride with carbon monoxide at 2000 lb./in.^{2} for 22 hr. gave a 97% crude yield of the chlorothiolformate (88% yield after distillation). Reactions under low pressure ($<$ 1000 lb./in.^{2}) still contained unreacted benzenesulphenyl chloride after 16 hr.

Dimethylene bischlorothiolformate ($\mathrm{(ClOCS\cdot\!-CH_2\!-)_2}$ was prepared by shaking a $\mathrm{CCl_4}$ solution of the (bis-sulphenyl chloride)† with 1000 lb./in.^{2} CO for 23 hr. The n.m.r. spectrum showed the complete absence of the sulphenyl chloride singlet (3·57 p.p.m.) and the formation of a new singlet (3·38 p.p.m.) which comprised 90% of the n.m.r. integral. I.r. analysis showed strong absorptions at 5·68 and 5·98 μ characteristic of chlorothiolformate. The product underwent extensive decomposition upon distillation *in vacuo*.

Electronegatively substituted sulphenyl chlorides such as 2,4-dinitrobenzenesulphenyl chloride and trichloromethanesulphenyl chloride did not incorporate any carbon monoxide after more than 24 hr. contact with 6000 lb./in.^{2} carbon monoxide (25°). Dimethylaminosulphenyl chloride also failed to react with CO under these conditions.

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