cis-2-Chlorovinyl Ketones

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2-CHLOROVINYL KETONES RCO·CH:CHCl have been prepared in various ways.[1] The compounds obtained by addition of acyl chlorides to acetylene or by chlorination of acylacetaldehydes have the *trans*-configuration (I), as has been shown by chemical[2,3] and spectroscopic[4] tests. In all probability the other syntheses known also give the same *trans*-isomers.

The *cis*-isomers have not yet been described, despite the fact that there is a vast literature[1] on the chemistry of 2-chlorovinyl ketones and in particular on the easy nucleophilic substitution of halogen. For this reason it has not hitherto been possible to carry out a rigorous study of the mechanism and stereochemistry of the nucleophilic substitutions in this vinylic system.

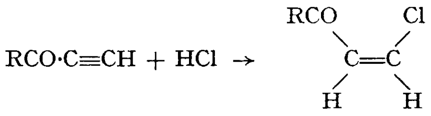
cis-2-Chlorovinyl ketones (II) have now been prepared by addition of the stoicheiometric quantity of hydrogen chloride to ethynyl ketones (III) in anhydrous chloroform at −40° and in the presence

TABLE

Data on representative compounds p-R'C_6H_4·CO·CH : CHX

R'	X		*trans* M.p.	$\nu_{C=O}$(cm.$^{-1}$)	$\nu_{HC=CH}$(cm.$^{-1}$)		*cis* M.p.	$\nu_{C=O}$(cm.$^{-1}$)
H	Cl	(I)	22—23°	1670	930	(II)	4—5°	1670
OMe	Cl	(I)	49—50°	1665	927	(II)	27—28°	1670
Cl	Cl	(I)	35·5—36°	1665	932	(II)	31—32°	1675
H	SPh	(IV)	76—77°	1655	940	(V)	80—81°	1645
OMe	SPh	(IV)	70—71°	1650	942	(V)	107—108°	1645
Cl	SPh	(IV)	61—62°	1650	940	(V)	125—126°	1645
H	SO_2Ph	(VI)	113°	1680	955	(VII)	146—147°	1680

of CuCl catalyst. Conversion is complete in 6—24 hr. The *cis*-configuration is confirmed by the absence in the infrared spectrum of the strong band at 930—935 cm.$^{-1}$, which is present in the *trans*-isomers (I). Small quantities of *trans*-isomers are easily removed by crystallisation of the crude products from ethyl ether–light petroleum. A slight excess of acid or a higher reaction temperature results in *cis*- → *trans*-inversion.



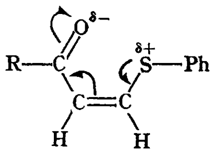
$$\mathrm{RCO{\cdot}C{\equiv}CH} + \mathrm{HCl} \rightarrow (\mathrm{RCO})(\mathrm{H})\mathrm{C{=}C}(\mathrm{Cl})(\mathrm{H})$$

(III) (II)

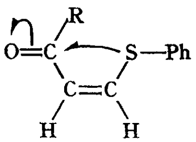
In both series of 2-chlorovinyl ketones (I) and (II) nucleophilic substitution of halogen with thiophenate ion in acetone–water at 0° proceeds with retention of configuration, yielding phenylthiovinyl ketones, R·CO·CH : CH·SPh, *trans*- (IV) and *cis*- (V) respectively: the first contain on average 5% *cis*-isomer; the second are sterically pure. The stereochemical course of the reaction is analogous to that which is generally observed in 2-halogeno-ethylenes activated by electron-withdrawing groups in the 1-position, at least in the substitutions by anionic reagents with a high carbon nucleophilicity.[5] This seems to indicate that the substitution proceeds *via* nucleophilic attack on the 2-carbon and synchronous displacement of halogen.* A fuller investigation of the reaction mechanism is in process.

The *trans*-sulphides (IV) are thermodynamically less stable than the *cis*-isomers (V) and are converted into the latter by base catalysis. In accordance with this, a slight excess of base will bring about the formation of *cis*-sulphides (V) in nucleophilic substitutions starting from *trans*-2-chlorovinyl ketones (I). *cis*-Sulphides can also be obtained by base-catalysed addition of thiophenol to ethynyl ketones (III). The oxidation of sulphides (IV) and (V) with peracids produces *trans*- and *cis*-sulphones (VI) and (VII) respectively. Of these, the *trans*-isomers (VI) are thermodynamically more stable. Physical properties of representative compounds are reported in the Table.

The relative stability of the *trans*- and *cis*-sulphones can be rationalised in terms of electrostatic and steric repulsion between the carbonyl and sulphonyl groups. Intramolecular interactions between the sulphur atom and the carbonyl group, as in (Va) or in (Vb), may contribute to the greater thermodynamic stability of the *cis*-sulphides (V).



(Va)



(Vb)

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* The stereochemistry of the substitution in the *cis*-series could be equally justified by an elimination–addition mechanism.

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[4] W. R. Benson and A. E. Pohland, *J. Org. Chem.*, 1964, **29**, 385.

[5] S. Patai and Z. Rappoport, "The Chemistry of Alkenes", ed. S. Patai, Interscience, London, 1964, p. 525.