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HALOGENATED KETENES XVII[1] ON THE STEREOCHEMISTRY OF THE CYCLOADDITION OF ALDOKETENES TO CHLORAL.

William T. Brady and Larry Smith,

Department of Chemistry, North Texas State University, Denton, Texas

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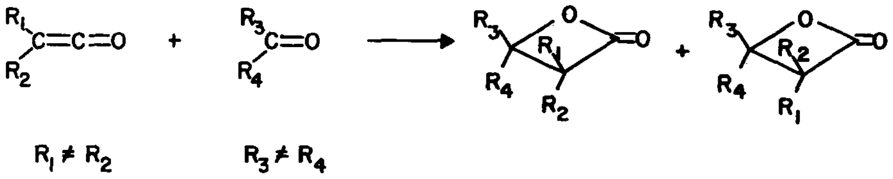
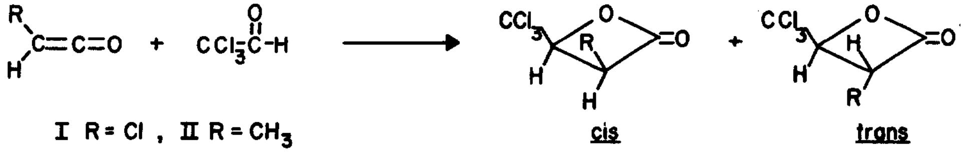
There have been numerous reports of the cycloaddition of ketenes to carbonyl compounds to produce 2-oxetanones.[2] However, reports of cycloadditions of ketenes to carbonyl compounds in which geometrical isomers could be produced have been rare and no stereochemistry has been described for this reaction.[3]



The cycloaddition of aldoketenes to olefins, a concerted process, is stereoselective to produce the cis-cyclobutanone.[4-6] The cycloaddition of aldoketenes to imines has been shown to be a two-step process and yields only trans-2-azetidinones.[7] As a preliminary to a study of the mechanism of ketene - carbonyl cycloadditions, we wish to report the steric course of this reaction using two aldoketenes.

The cycloaddition of chloro- and methylketene to chloral produces cis- and trans-4-trichloromethyl-2-oxetanones.



Thus, 132 mmol of triethylamine in 50 ml of hexane was slowly added at 25° C. to a solution of 150 ml of hexane, 132 mmol of chloroacetyl chloride and 153 mmol of chloral. After four hours, the solution was filtered, concentrated and distilled to yield (40%) of a mixture of cis- and trans-I as evidenced by vpc. Fractional distillation of the mixture gave fractions containing both isomers at 40-43° (1.0 mm) which were identified by nmr: ir, 1870 cm.$^{-1}$ (C=O)· nmr (CDCl$_3$), cis-I, pair of doublets centered at δ5.18 and δ5.58 (J = 6.0 cps); trans-I, pair of doublets centered at δ5.04 and δ5.25 (J = 3.0 cps). A higher fraction (46° at 1.0 mm) contained only trans-I; nmr (CCl$_4$), pair of doublets centered at δ5.22 and δ5.44 (J = 3.0 cps). Calcd. for $C_4H_2Cl_4O_2$: C, 21.46; H, 0.90. Found· C, 21.48; H, 1.02. The cis-I/trans-I ratio in the reaction mixture was 1.64 as determined by vpc.

Similarly the dehydrochlorination of propionyl chloride at 25° in the presence of chloral produced a mixture of cis- and trans-II (43%) at 50-54° (0.2 mm); ir, 1870 (C=O); nmr (CCl$_4$), cis-II, δ1.55 (d), δ4.2 (m) and δ5.08 (d, J = 6.75 cps); trans-II, δ1.55 (d), δ3.81 (m) and δ4.77 (d, J = 3.24 cps) Cis-II was obtained pure by fractional distillation (56° at 0.2 mm); nmr (CCl$_4$), δ1.53 (d, 3H), δ4.08 (q, 1H) and δ4.98 (d, 1H, J = 6.75 cps). Calcd. for $C_5H_5Cl_3O_2$· C, 29.52; H, 2.48. Found· C, 29.66; H, 2.46. The cis-II/trans-II ratio in the reaction mixture was 1.39 as determined by vpc

A characteristic reaction of 2-oxetanones is the thermal elimination of carbon dioxide producing an olefin.[8] When heated at 160° for six hours, I and II showed no evidence of olefin formation. The original samples were recovered in > 95%. This thermal stability is in contrast to that of 3,3-dichloro-4,4-dimethyl-2-oxetanone, which yielded 50% of 1,1-dichloro-2-methylpropene, (bp 108-110°; ir, 1630 cm.$^{-1}$ (C=C)), after two hours at 150°.[9] The preparation of this oxetanone was accomplished in 30% yield by the dehalogenation of trichloroacetyl chloride with zinc in acetone; bp 34° at 0.5 mm; mp 24°; ir, 1875 cm.$^{-1}$ (C=O); nmr (CCl_4), δ 1.79. Calcd for $C_5H_6Cl_2O_2$: C, 35.53 H, 3.58. Found: C, 35.76; H, 3.47.

Thus, cycloadditions of chloro- and methylketene to chloral have been shown to give *cis*- and *trans*-2-oxetanones. That the *cis* isomers are formed and, moreover, that these isomers predominate, strongly suggests the cycloaddition occurs by a concerted process. A stepwise process would be expected to produce the sterically favored *trans* isomers.

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