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HALOGENATED KETENES. III. METHYLCHLOROKETENE[1]

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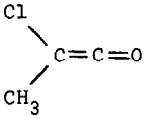
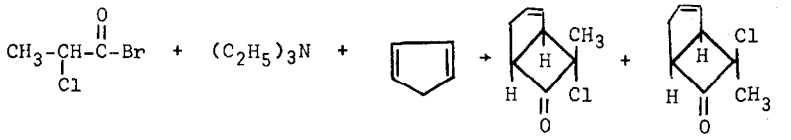
There are some reports in the older literature on the preparation of ethylchloro-, methylbromo-, and ethylbromoketenes, but these ketenes reportedly polymerized very rapidly and no work on cycloaddition reactions was indicated (3,4,5). There appears to have been no further work reported on alkylhaloketenes. In connection with a definitive study of halogenated ketenes, we became interested in the synthesis and cycloaddition reactions of this type of ketene. The present communication describes the synthesis and some chemistry of methylchloroketene.



This ketene was prepared by the dehydrobromination of α-chloropropionyl bromide. 7-Chloro-7-methylbicyclo[3·2·0]hept-2-en-6-one (6), as prepared from methylchloroketene and cyclopentadiene, is a mixture of cis and trans isomers in the ratio of 3:1 respectively as determined by n.m.r. (7) and g.l.p.c. (8). Fractionation gave a fraction high (91%) in the cis isomer and a second fraction high (90.5%) in the trans isomer. Efforts to form a cycloadduct of methylchloroketene with cyclohexene, an unactivated olefin, were unsuccessful. Apparently, this ketene unlike dichloroketene is not reactive with unactivated olefins,

at least under the conditions investigated (9). N-Benzyl-2-chloropropionamide was prepared by treating the ketene with benzylamine thus yielding some information about the stability of methylchloroketene in the reaction mixture. Methylchloroketene was generated <u>in situ</u> in the presence of cyclopentadiene.



<u>cis</u> isomer <u>trans</u> isomer

Thus, α-chloropropionyl bromide (0.15 m.) in 25 ml. of hexane was added dropwise to a solution of triethylamine (0.18 m.) and cyclopentadiene (1.5 m) in 100 ml. of anhydrous hexane at 0-5°C. The amine salt was removed by filtration and distillation at reduced pressure afforded the adduct in 77% yield. Analysis by g.l.p.c. of the reaction solution showed an isomer distribution of 3:1. Careful fractionation of the adduct through a 6 in. vigreaux column yielded a fraction (91%) at 70-72° at 5 mm. and a higher boiling fraction (90.5%) at 80-82° at 5 mm. There was no evidence of isomerization on standing at room temperature for 2 weeks. Infrared absorption (smear) of both isomers: 1800 $cm.^{-1}$ (s) and 1605 $cm.^{-1}$ (w); n.m.r. spectrum ($CHCl_3$) for the low boiling isomer: multiplet centered at 5.9 p.p.m., multiplet centered at 4.3 p.p.m., multiplet centered at 3.8 p.p.m., multiplet centered at 2.6 p.p.m., singlet at 1.8 p.p.m. (due to high boiling isomer, 9%) and a singlet at 1.5 p.p.m. These peak areas (excluding the one at 1.8 p.p.m.) were in the ratio of 2:1:1:2:3; n.m.r. spectrum ($CHCl_3$) for the high boiling isomer: multiplet centered at 5.9

p.p.m., complex multiplet centered at 3.7 p.p.m., multiplet centered at 2.6 p.p.m., singlet at 1.8 p.p.m. and a singlet at 1.5 p.p.m. (due to low boiling isomer, 9.5%). The peak areas (excluding the one at 1.5 p.p.m.) were in the ratio of 2:2:2:3. Calcd. for C_8H_9ClO: C, 61.35; H, 5.79. Found: C, 61.13; H, 6.11. Mol. Wt. 169 (theory 156).

The chemical shift of the methyl group indicates that the low boiling isomer has the methyl group over the double bond and the high boiling isomer has the chlorine atom over the double bond. Consequently, each isomer in chloroform was treated with bromine at room temperature and an n.m.r. determination made. The spectrum of the high boiling isomer was unchanged. However, the spectrum of the low boiling isomer was altered. There was a new singlet at 1.9 p.p.m. An examination of a molecular model of the cis isomer shows that the methyl group lies over the double bond, and therefore falls into the shielding cone associated with this π-electron system. A similar case has been observed in a steroidal ethynyl-ethylenic acetate (10). Therefore, this must mean that the low boiling isomer is the cis isomer and the high boiling isomer the trans isomer.

Methylchloroketene was prepared as described above in the absence of the cyclopentadiene. One hour after the addition was complete, a stoichiometric amount of benzylamine was added with stirring. Filtration of the reaction mixture yielded a quantitative amount of triethylammonium bromide. The filtrate was washed with dilute acid, water and finally dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent yielded N-benzyl-2-chloropropionamide in 55% yield. Upon recrystal-

lization from hexane this material has a m.p. of 78-79°C. The literature m.p. is 80-82°C (11).

An examination of molecular models of methylchloroketene and cyclopentadiene does not reveal an explanation for the isomer distribution of 3:1. Therefore, it seems likely that the initial attack of the diene on the ketene is not responsible for this distribution but rather a second ring closing step determines the distribution. This is consistent with the findings of Bartlett and coworkers regarding the cycloaddition of haloolefins. Namely, a two-step mechanism *via* a bifunctional intermediate is necessary to account for the isomer distribution (12).

The preparation of methylchloroketene in the absence of cyclopentadiene is very noteworthy. This experiment indicates the ketene is not immediately polymerized in the presence of the amine salt and that the ketene can be isolated in solution for subsequent work. Our studies on the synthesis and cycloaddition of alkylhaloketenes are continuing.

ACKNOWLEDGEMENTS

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