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STEREOCHEMISTRY OF POLAR ADDITIONS TO ACETYLENES

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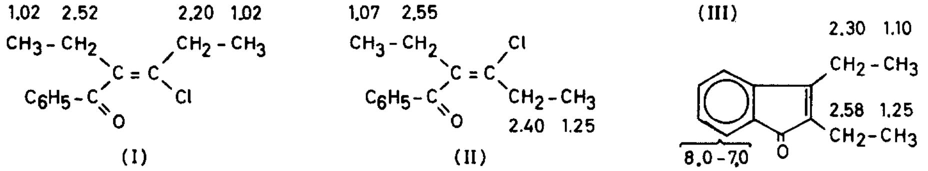
The addition of Friedel Crafts acid chloride - $AlCl_3$ complexes to acetylenes, leads to the formation of β-chlorovinyl ketones, which are very useful intermediates for the synthesis of quite a variety of compounds (1)(2). Though a lot of preparative information is given, very little work has been done on the mechanism of these additions. Several studies have shown that β-chlorovinyl ketones prepared from acetylene have the trans configuration (3), but this type of β-chlorovinyl ketones is extremely sensitive to isomerisations (4). For the more stable β-chlorovinyl ketones, prepared from dialkylacetylenes, the cis-trans proportion has not been determined, as far as we know. Kroeger, Sowa and Nieuwland (5) reported the addition of acetyl chloride to 3-hexyne, with $SnCl_4$ as condensing agent, but they made their stereochemical assignments on basis of the boiling point and on the immediate precipitation of NaCl from the trans isomer with an alcoholic solution of NaAc. We performed the addition of benzoyl chloride - $AlCl_3$ complex and a few other acid chloride - $AlCl_3$ complexes, to 3-hexyne, isolated the cis and trans isomers and determined their relative proportions. As it has been demonstrated by control experiments that the isolated β-chlorovinyl ketones are stable to the reaction conditions, the information on the kinetically controlled product compositions enables us to propose a reaction mechanism.

The addition of benzoyl chloride - $AlCl_3$ to 3-hexyne was performed with equimolecular amounts of the reactants in dichloromethane at room temperature. The reaction was instantaneous and quantitative. Examination of the reaction mixture by GLC revealed three components. A TLC analysis confirmed these results. The three products were isolated by preparative GLC and preparative TLC. Twoof these products could be characterised as β-chlorovinyl ketones. The cis and trans structure was assigned from the NMR spectra. The trans isomer (II) has one ethyl group cis of the carbonyl ; the protons of this group exhibit a resonance at 0.2 ppm lower field than the corresponding protons in the cis isomer (I).

Scheme I :



The third product has been identified as the 2,3 diethyl-indenone (III). The IR and UV data correspond with those of Bergmann (6), and NMR and MS spectral data are in complete agreement with the proposed structure.

By lowering the reaction temperature to -40°C, the reaction could be followed. The reaction mixtures were analysed by GLC analysis of the benzoyl chloride (as ethylbenzoate) and of the products, by measuring their peak areas against the peak area of an internal standard product of known concentration. The reaction followed first order kinetics for both the 3-hexyne and the benzoyl chloride - $AlCl_3$ complex.

The GLC analysis showed the following product composition :(I) : 80% ; (II) : 12% ; (III) : 8%. The pure trans and cis isomers, in the presence of $AlCl_3$ at -40° C in dichloromethane, did not lead to the formation of any indenone.

By changing the solvent from pure dichloromethane to a mixture of dichloromethane-benzoylchloride (50/50) with higher polarity, the per cent of trans isomer and of indenone increased respectively to 28,5% and 13,5% ; the per cent cis isomer decreased to 58%. The addition of acetyl chloride - $AlCl_3$ complex to 3-hexyne resulted in the predominant formation of trans isomer: 75% of the trans isomer and 25% of the cis isomer. Propionyl chloride - $AlCl_3$ complex reacted with 3-hexyne to form 64% cis isomer, 26% trans isomer and 10% 1,2-diethylcyclopent-1-en-3-one.

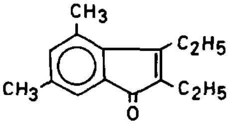
p-Methylbenzoyl chloride - $AlCl_3$ complex and 3-hexyne gave almost exclusively the cis-β-chlorovinyl ketone. With 2,4,6-trimethylbenzoyl chloride a very unstable reaction mixture was obtained and the various products converted into one another.

In all these cases there is a correlation between the per cent of trans isomer and of cyclisation products, and the relative ease of ionization from the donor-acceptor complex to a more ionic species.

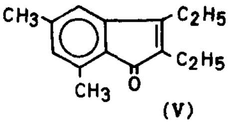
Thus infra-red investigations of the solid benzoylchloride - $AlCl_3$ complex showed only the donor-acceptor complex (7). Also by spectroscopic methods, it was shown that the acetyl chloride - $AlCl_3$ complex exists as a mixture of the oxocarbonium salt and the polarised covalent complex, in which the $AlCl_3$ is coordinated with the oxygen atom of the carbonyl group (8). However high resolution NMR investigations by Olah and coworkers (9) showed that the acetyl chloride - $AlCl_3$ complex in dichloroethane, in pure acetyl chloride and in nitromethane, contains no detectable amounts of oxocarbonium ions. Cryoscopic measurements of the ionic $CH_3CO^+SbF_6^-$ complex in nitromethane, showed negligible if any ion separation (9). Thus even in their ionic form, no free ions are observed. Furthermore, a different behaviour for the $CH_3COCl.SbCl_5$, $CH_3CH_2COCl.SbCl_5$ and $C_6H_5COCl.SbCl_5$ complexes was reported by Olah (10) : the first complex appears to be a $CH_3CO^+SbCl_6^-$ compound, but the last two complexes are donor-acceptor complexes and contain only a very small amount of the ionic form.

More recently, Tomalia (11) investigated a number of aryl oxocarbonium ions by NMR and reported the per cent of ionization of the aromatic acid chlorides to their respective oxocarbonium ions, in fluorosulfonic acid : 3,5-dimethylbenzoyl chloride (48%) , p-methylbenzoyl chloride (0%) and 2,4,6-trimethylbenzoyl chloride (100%).

For reactions performed with 3,5-dimethylbenzoyl chloride, $AlCl_3$ and 3-hexyne in dichloromethane, the per cent of indenone increased to 38,7%, whereas the reaction mixture contained also 56,9% cis and 4,4% trans isomer. By activation of the ortho position next to the carbonyl group, the ring closure with the formation of indenone is favored as expected. Moreover, the following important observation has been made, on basis of the NMR spectrum of the indenone : the δ-values of the aromatic protons (6,74 ppm and 6,92 ppm) seem to exclude the 2,3-diethyl-4,6-dimethyl-1-indenone (IV). Considering the literature data about indanones (12) and the NMR data of the 2,3 diethyl-indenone (III), a 2,3-diethyl-5,5-dimethyl-indenone (V) is proposed.

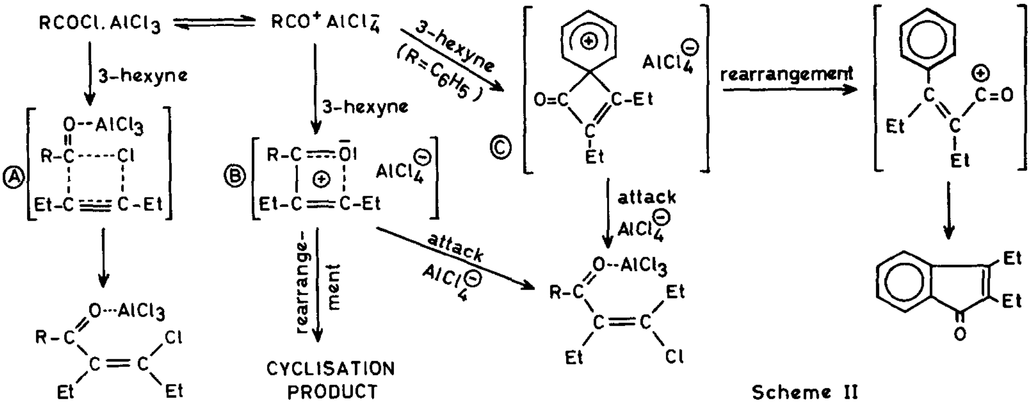


(IV)



(V)

On basis of the above results, it seems reasonable to us to conclude that the donor-acceptor complex leads to the cis isomer along the intermediate A (Scheme II) and that the more ionic form (maybe present at low concentration) is responsible for the trans isomer and the cyclisation products. The following reaction scheme can be proposed :



Scheme II

For aliphatic acid chlorides the intermediate B would lead to the trans isomer by an appropriate attack of $AlCl_4^-$, displacing the C-O bond.

For aromatic acid chlorides, a spirophenonium ion C similar to the intermediate proposed in the acid catalysed rearrangement of vinyl ketones (13) seems to be favoured as intermediate. By appropriate attack of $AlCl_4^-$ again the trans product would be formed, whereas on rearrangement an indenone derivative would result. This rearrangement could explain the structure of the indenone formed in the reaction of 3,5-dimethylbenzoyl chloride and 3-hexyne.

For further elucidation, kinetic measurements for stereospecific trans addition are now in progress together with experiments wherein substrate and catalyst are changed.

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