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PHOTOCHEMICAL LOSS OF A CHLORIDE ANION FROM AN α-CHLOROKETONE.
THE PHOTOLYSIS OF EXO-3-CHLOROBICYCLO[2.2.1]HEPT-5-EN-2-ONE IN METHANOL.

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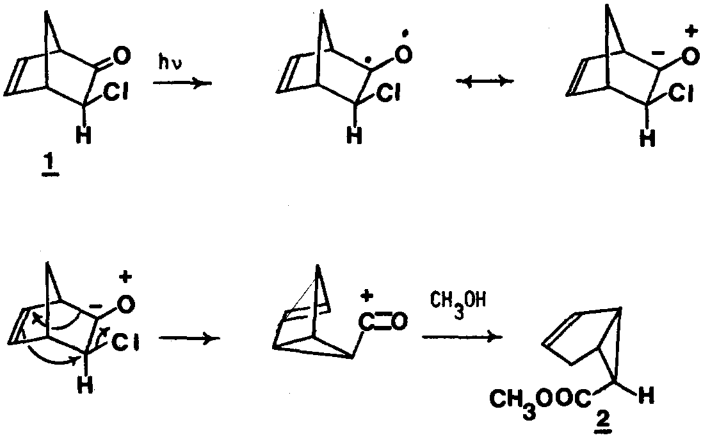
In the course of our investigations on the photochemistry of α-chloroketones we have photolyzed exo-3-chlorobicyclo[2.2.1]hept-5-en-2-one (1). Ketone 1 when photolyzed in methanol (0.05 M, 1) through a pyrex filter with Rayonet 3000 Å lamps results in the stereospecific formation of endo-6-carbomethoxybicyclo[3.1.0]hex-2-ene (2) in greater than 95% yield. The structure of 2 was shown to be correct by comparison of the nmr and ir spectra of 2 with an authentic sample.[1] The quantum yield for the formation of 2 was found to be 0.8 using a benzophenone-benzhydrol actinometer.[2]

The formation of 2 from 1 involves the photochemical loss of a chloride anion. While the loss of a chloride anion has precedent in the photolysis of several dichloromethylcyclohexadienones in nucleophilic solvents, the nature of the excited state and mechanisms were not clear.[3,4] For this reason we have investigated and now report the nature of the excited state in the conversion of 1 into 2 and also propose a mechanism for this reaction.

In an attempt to determine the photochemically reactive state of 1 leading to 2 a quenching study was carried out. The results indicated that this reaction could not be quenched by 2M piperylene. The photochemically reactive state leading to the formation of 2 must therefore be either an excited singlet or a very rapidly decomposing (unquenchable) triplet. When 1 was photolyzed in the presence of the triplet sensitizer acetophenone the formation of 2 was almost completely suppressed. Thus we can conclude that the singlet excited state of 1 leads to 2.

The mechanism that we envision for the conversion of 1 into 2 begins with the excitation of the carbonyl group (n, π*) of 1. In the excited state of 1 the partial positive charge on the oxygen of the carbonyl group is attenuated because a non-bonding electron largely localized on oxygen is excited into a π antibonding MO. This shift of electrons would be expected to decrease the dipole moment of the carbonyl group. Measurement of the dipole moment of formaldehyde shows a decrease from 2.5 D(S_0) to 1.5 D(S_1 and T_1).[5] According to resonance theory we are able to write two contributing forms for the excited state, one of which has carbon negatively charged and oxygen positively charged. If the C-Cl bond of 1 were broken in the photoexcited state, the carbonium ion or incipient carbonium ion would be more stable than if it were formed in the ground state because in the excited state the carbon alpha to the C-Cl bond bears a partial negative charge. Thus the fact that 1 is photochemically labile at 35° whereas it is thermally stable in a sealed tube at 100° can be understood in terms of the electronic configuration of the carbonyl group of 1 in the excited state vs the ground state. A mechanism leading to the formation of 2 from 1 is outlined below.



We are presently investigating a series of other chloroketones in an effort to understand the exact stereoelectronic requirements necessary for the photochemical loss of chloride anions from ketones.

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