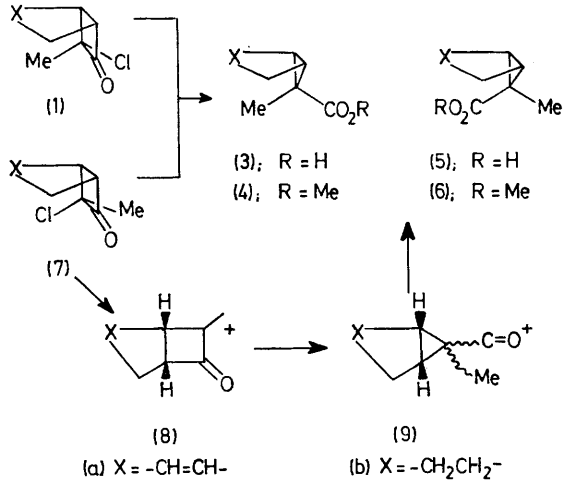
Photochemical Ring Contraction–Solvolysis in the 7-Chloro-7-methylbicyclo[3.2.0]heptan-6-one Series. A Linked Dependence on Configuration and Conformation

By GUILFORD JONES, II* and LORRAINE P. MCDONNELL
(*Department of Chemistry, Boston University, Boston, Mass.* 02215)

Summary On photolysis in methanol the stereoisomeric 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-ones and their saturated analogues give the cyclopropylesters (**4**) and (**6**); the importance of ring contraction—solvolysis depends on the conformational preferences of the *exo*- and *endo*-stereoisomers.

THE photochemistry of cyclobutanones in solution is now well understood[1] in terms of three principal competing processes: (1) cycloelimination to give a keten and an olefin; (2) ring expansion to give a trappable oxacarbene intermediate; and (3) decarbonylation to form a cyclopropane. We now report a photochemical reaction of



previously unrecognized significance for α-chlorocyclobutanones,[2] which is analogous to the Favorskii rearrangement and which is strikingly dependent on stereochemistry.

Photolysis of (**1a**) in methanol (450 W medium pressure Hg lamp, Pyrex filter) to 60% conversion gave three products in a 6 : 2 : 1 ratio. One of the minor components was identified as an isomer of methyl 7-chloro-octa-4,6-dienoate (**2**) on the basis of n.m.r., i.r., u.v., and m.s. data. None of the photoproducts was produced in the dark but treatment of (**1a**) with NaOH in methanol[3] gave (**3a**). Diazomethane esterification gave (**4a**)[4] which was identical to the other minor photolysis product. The principle photoproduct (**6a**)[4] was saponified giving (**5a**) which was identical to the base-catalysed ring contraction product of (**7a**).[3] Treatment of an aqueous extract of the photolysate with $AgNO_3$ confirmed the presence of chloride ion, formally accompanying (**4a**) and (**6a**).

TABLE. Quantum yields for photolysis of cyclobutanones in methanol[a]

Starting Cyclobutanones (λ_{max}/nm)	ϕ (**6**)	ϕ (**4**)	ϕ (**2**)
(**1a**) (318)	0·59	0·14	0·09
(**7a**) (304)	0·19	0·04	0·72
(**1b**) (318)	0·48	0·28	—
(**7b**) (293)	0·31	0·02	—

[a] Rayonet reactor (300 ± 30 nm, Pyrex tubes), 30 ± 1°C, 0·06 M ketone, valerophenone actinometer;[5] conversion of ketone and actinometer <10%; standard deviations in replicate measurements indicated an error of ±10% for ϕ (**6**) and ±20% for ϕ (**2**) or (**4**).

On photolysis in methanol (**7a**) gave only small amounts of the ring contraction–solvolysis products, (**4a**) and (**6a**), and predominantly an isomer of (**2**) different from that derived from (**1a**).† The saturated ketones (**1b**) and (**7b**) on photolysis in methanol gave (**4b**) and (**6b**) each of which could be prepared independently from (**1b**) and (**7b**),[3] by stereospecific base-catalysed ring contraction and esterification. Long chain esters, analogous to (**2**) were tentatively identified by g.l.c.–m.s. as the major and minor photoproducts from (**7b**) and (**1b**), respectively.

† Stereospecific photocycloelimination followed by solvent capture is well known.[1]

Quantum yields for the photolysis of (**1**) and (**7**) to low conversion (Table), are high and undiminished in the presence of 2,5-dimethylhexa-2,4-diene. A pattern of stereochemical dependence can be seen. Ring contraction–solvent incorporation is favoured by *exo*-chloro substitution in the ketone and is modestly stereoselective [for (**1**) in a direction opposite to the base-catalysed reaction‡].

From the nature of the products (a 1,2 rearrangement and a nucleophilic addition are required) and the literature precedent for ionization of excited ketones α-substituted with a good leaving group,[7] a mechanism for ring contraction–solvolysis involving singlet excited ketones and the cations (**8**), which partition to the acylium ions (**9**)§ followed by trapping by methanol, is suggested.¶

Photoexcited (singlets[1]) (**1**) favour ionization rather than cracking, compared with (**7**), where steric inhibition to the departure of chloride is expected. The ground state conformation also may affect partitioning of the excited state. The n, π^* transitions for the ketones (Table) indicate a preference for axial chlorine in (**1**). The bathochromic shift has been noted previously for cyclobutanones[10] and has been treated theoretically.[11] The conformational preference can affect the ground state chemistry of the alkylchloroketen–cyclopentadiene adducts.[3] A probable factor then in the destruction of the excited chlorocyclobutanones is the availability of conformations with axial chlorine which react before conformational equilibration.[12] This conformational control of photoionization has been noted for α-tosyloxyketones[7a] and may be general.

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‡ Ring contractions of (**1a**) and (**7a**) catalysed by base under a variety of conditions have been reported,[5] none of which give product distributions identical to those found under photolysis conditions.

§ Cyclopropyl acylium ions are formed readily in solution[8] and even isolated,[9] resist ring opening and decarbonylation, and are trapped by alcohols to form esters.[9] The preference for (**4a**) from (**1a**) and (**7a**) could reflect homoaromatic stabilization of the *endo*-acylium unit by the proximate π-system.

¶ Not to be ruled out for a portion of the reaction is a mechanism involving ring contraction concerted with (equatorial) departure of chloride, analogous to the base-catalysed rearrrangement,[3] which would lead to major and minor cyclopropyl ester products for (**7**) and (**1**), respectively.

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