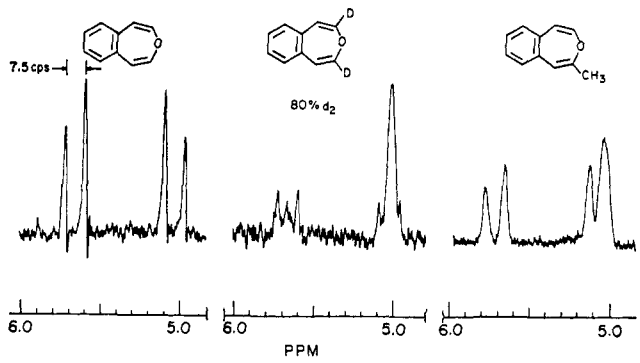

Figure 1. Nmr spectra of compounds **1a**, **1b**, and **1c** in deuteriochloroform; scale is parts per million downfield from internal tetramethylsilane.

oxepin itself[9] should not be observed.[2] Consequently we attribute the downfield portion of the $(AB)_2$ pattern to the protons adjacent to the oxygen (α hydrogens) and the upfield portion is assigned to β hydrogens. If the assumption is correct, the spectra show that substituents attached to bridgeheads in the starting materials appear in α positions in the benzoxepins. This skeletal change is easily explained by mechanistic sequence **1** → **2** → **3** and is difficult to rationalize by any mechanism involving bond breaking and migration of groups by 1,2 shifts. We believe that the change **1** → **2** is the first example of an intramolecular 6 + 2 cycloaddition.[10]

Under the conditions of irradiation described above, the oxepins appear to be the only primary photoproducts formed in direct excitation experiments. However, high conversions cannot be obtained because of competitive absorption of light by the reaction products, a process shown in separate experiments to lead to slow photochemical destruction of the benzoxepins. However, the reaction can be used in its present state of development for small-scale preparation of benzoxepins because of the ease of separation of the products. During chromatography on silica gel, the starting materials undergo quantitative rearrangement to α-naphthol (or 4-methyl-1-naphthol) which is held very strongly on the absorbent. Work designed to elucidate further the detailed mechanism of the excitation and decay processes is in progress.

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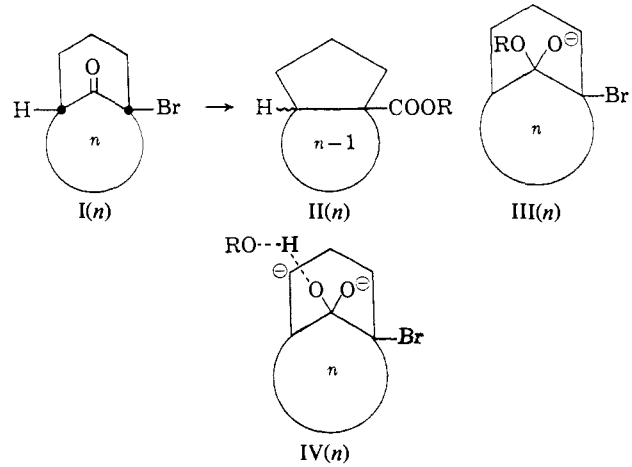
Mechanistic Changes in a Favorskii Reaction[1]

Sir:

It is well established that the Favorskii reaction of α-halo ketones can proceed by different mechanisms. Compounds with an α'-hydrogen atom may rearrange by a path involving an intermediate formed by loss of both α-halogen and α'-hydrogen atoms (normal Favorskii reaction),[2] whereas ketones without an α' hydrogen probably rearrange by the semibenzilic mechanism (quasi-Favorskii reaction) originally suggested by Tchoubar and Sackur.[3] While considerable effort has been devoted to defining the exact nature of the "symmetrical" intermediate(s) in the normal Favorskii reaction,[4] little attention has been given to the possibility that the semibenzilic mechanism could also be operating in these reactions,[5] even though at least one compound with an acidic α' hydrogen (2-bromocyclobutanone) has been found to rearrange by a route not involving a symmetrical intermediate.[6] We wish to report a demonstration that an α-halo ketone with an α'-hydrogen atom can undergo rearrangement either by way of a symmetrical intermediate or by way of a semibenzilic intermediate III depending on the experimental conditions.

The rearrangement of *cis*-I(6)[7] and its next higher homologs *cis*-I(7) and *cis*-I(8)[8] was examined for deuterium incorporation, product stereochemistry, and the fate of optical activity. The results of this study allow an unambiguous distinction between a cyclopropanone (or equivalent) and a semibenzilic intermediate. A semibenzilic path requires retention of optical activity and either no incorporation of C-D into II, or else deuterium exchange in I before rearrangement. The intermediacy of a cyclopropanone requires both incorporation of C-D into II and racemization of optically active bromo ketone [I(7) or I(8)];[9] deuterium in-



n = six, seven, or eight total carbon atoms in the ring

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(5) Provided that the semibenzilic mechanism predicts the correct product structure and provided that epoxy ether formation is not faster.
(6) C. Rappe, *Acta Chem. Scand.*, **21**, 163 (1967).
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(8) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Org. Chem.*, **32**, 2664 (1967).

Table I

Expt	Bromo ketone	Reagent	Solvent[a]	Product	% yield	Atoms of D[b]	Mechanism
1	I(6)	NaOD	EtOD–D_2O	II(6), R = H	95	0.00	Semibenzilic
2	I(6)	KO-*t*-Bu	*t*-BuOD	II(6), R = *t*-Bu	94	0.026	Semibenzilic
3	I(7)	NaOD	EtOD–D_2O	II(7), R = H	80	0.01	Semibenzilic
4	I(7)	NaOMe	MeOD	II(7), R = Me	96	0.00	Semibenzilic
5	I(7)	KO-*t*-Bu	*t*-BuOD	II(7), R = *t*-Bu	67	0.83[c]	Cyclopropanone
				Recovered I(7)		0.00	
6	I(7)	$AgNO_3$	EtOD–D_2O	II(7), R = H	85	0.00	Semibenzilic
7	I(8)	NaOD	EtOD–D_2O	II(8), R = H	88	0.90[c]	Cyclopropanone[d]
8	I(8)	$AgNO_3$	EtOD–D_2O	II(8), R = H	25	0.005	Semibenzilic

[a] Reactions were carried out at the reflux temperature of the solvent except for reactions 6 and 8 which were done at room temperature. [b] Combustion deuterium analyses (per molecule of product) by J. Nemeth, Urbana, Ill. [c] Value expected for rearrangement entirely by a cyclopropanone when allowance is made for OH introduced into the solvent and for $k_H/k_D \sim 4$–5 in the irreversible carbanion protonation (T. Riley and F. A. Long, *J. Am. Chem. Soc.*, **84**, 522 (1962)). [d] An optically active sample of I(8), $[\alpha]^{19}D$ −10° (*c* 3.03, chloroform), was divided into two portions, one of which was rearranged in sodium hydroxide–ethanol–water to give 67% *cis*-II(8) of rotation $[\alpha]^{20}D$ +1.1° (*c* 6.20, chloroform), and the other was rearranged in the silver nitrate–ethanol–water reagent to give 52% *cis*-II(8) of rotation $[\alpha]^{19.5}D$ +31.3° (*c* 4.26, chloroform). The loss in optical activity shown by the product from the sodium hydroxide reaction corresponds to 96% racemization.

corporation alone is sufficient provided that no α'-hydrogen exchange occurs before rearrangement. With these criteria and the fact that the stereochemistry of II from all reactions was exclusively *cis*[10] (required by a semibenzilic path, permitted by cleavage of a cyclopropanone), the results shown in Table I were obtained.

Under typical Favorskii conditions (NaOD–D_2O–EtOD or NaOMe–MeOD) I(6) and I(7) rearrange by the semibenzilic path, but when the ring size reaches that of I(8), the α' hydrogen becomes comparable in acidity to that of α-chlorocyclohexanone, and rearrangement by the symmetrical path taken by the latter ketone[2] becomes faster. However, under other conditions I(8) can rearrange by the semibenzilic path as revealed by its reaction with silver nitrate. While this change of mechanism undergone by I(8) might be considered exceptional since silver nitrate is not a typical Favorskii reagent, the change from a semibenzilic intermediate for rearrangement of I(7) with hydroxide or methoxide as base to a symmetrical intermediate for reaction with *t*-butoxide must be regarded as occurring under normal basic Favorskii conditions. We have considered four possible causes for the change in mechanism: (a) difference in base strength, (b) inability to form dianion IV, conceivably a required intermediate for semibenzilic rearrangement, (c) insufficient concentration of anion III(7) (R = *t*-Bu) for rearrangement *via* III(7) to compete with cyclopropanone formation, and (d) change in solvent polarity. The fact that I(7) will rearrange with methoxide ion by a semibenzilic path excludes IV(7) as a *required* intermediate. Of the remaining three possibilities, at present we favor a since I(6) with *t*-butoxide undergoes rearrangement by the semibenzilic path.

The demonstration that I(7) and I(8) can each rearrange to a single product by either a semibenzilic or a cyclopropanone intermediate shows a delicate balance between the two mechanisms and suggests the possibility that the semibenzilic mechanism may be operating with other α-halo ketones bearing α'-hydrogen atoms, either in preference to or concomitant with a cyclopropanone mechanism. Operation of the semibenzilic path might even be involved in the explanation for the puzzling variation of inversion and retention found in certain Favorskii rearrangements.[4c,e,i]

During cyclopropanone formation from I(7), it is difficult to visualize the bromine atom in any conformation other than equatorial with respect to the cyclohexanone ring. Perhaps there do exist two routes to a cyclopropanone,[11] one being a concerted 1,3 elimination with loss of equatorial α' hydrogen and α bromine in the case of I(7),[12] and the other involving loss of axial halogen from an enolate anion.[4l] Finally, if it is accepted that a cyclopropanone is the intermediate in reactions 5 and 7,[4k] then the exclusive formation of *cis*-II(7) and *cis*-II(8) provides additional evidence for the stereochemistry of cleavage of cyclopropanones, *i.e.*, with complete retention of configuration in the solvents used.[13,14]

(9) Conformational equilibration and symmetrical solvation of the intermediate are assumed.

(10) Authentic samples of *cis*-II(6), -II(7), and -II(8) and *trans*-II(7) and -II(8), R = H, have been prepared and their methyl esters compared with product methyl ester by gas–liquid partition chromatography. The isomers are readily distinguished in each case.

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The Formation of the Pentafluorosilicate Anion in Dehydrofluorination Reactions

Sir:

The pentafluorosilicate anion has very recently been reported[1,2] in salts of the Ph_4As^+, Et_4N^+, and *trans*-$(Et_3P)_2PtCl(CO)^+$ cations. We wish to report our evidence[3,4] for the formation of this anion in dehydrofluorination reactions.

The reactions of silicon tetrafluoride were included in a general study of the dehydrofluorination of pri-

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