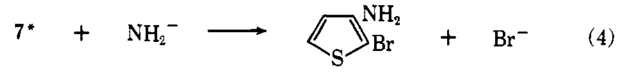
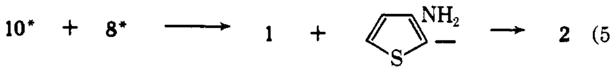
polybromothiophenes to 3-bromothiophene (**3**) under the conditions of run D.

A related and particulary significant observation is the rapid and complete reaction of each of the polybromothiophenes of Table I under the amination conditions of run A to produce 3-aminothiophene (**2**) in yields of up to 50%. Therefore not only the rearrangement (**1** → **3**) but also the cine-substitution (**1** → **2**) of 2-bromothiophene (**1**) may proceed by other than an elimination–addition mechanism. In fact, the exceptional stability of *o*-haloanions of five-membered heterocycles[18] and the recent reinterpretation[19] of the previous evidence[10,20] for the existence of five-membered hetarynes argue strongly against the intermediacy of arynes such as **5** in either of these reactions.[21]

A nonaryne mechanism for the cine-amination of 2-bromothiophene (**1**) which would account for all the data cited here and elsewhere[22] involves substitution of an activated[23] 3-bromine atom in one or several of the polybromothiophenes (**7***) present to give a 3-aminobromothiophene (**10***) (reaction 4[14]) which on subsequent transbromination (reaction 5[14]) would lead to the observed product, 3-aminothiophene (**2**). In support of this mechanism 2-bromo-4-aminothiophene can be



(4)[14]



(5)[14]

isolated in low yield from the reaction of 2-bromothiophene (**1**) with sodium amide and then converted to 3-aminothiophene (**2**) in 50% yield under conditions similar to run A.

Further details on this new mechanism as well as its applicability to other cases of cine-substitution *via* supposed aryne intermediates will be reported in subsequent publications.

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(18) For a summary, including significant unpublished data, see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press Inc., New York, N. Y., 1967, pp 290–291.

(19) Dissertations, University of Heidelberg, of V. Wahl (1962), H. Muller (1964), and M. Rings (1966); cited in ref 18, pp 291–292.

(20) G. Wittig, *Angew. Chem.*, **74**, 479 (1962).

(21) Hoffmann (ref 18, p 293) concludes that "no unambiguous evidence is as yet available for the formation of dehydro derivatives of five-membered aromatic heterocycles."

(22) H. W. Adickes, Dissertation, Texas Christian University, 1968.

(23) Reference 15, p 69.

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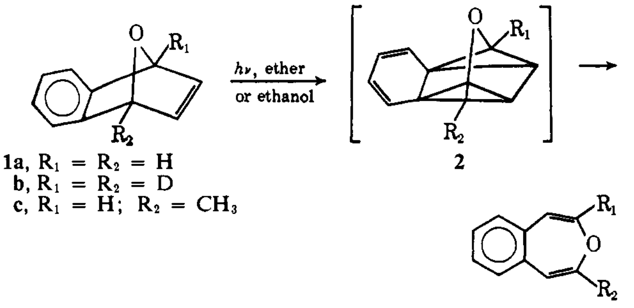
The Photorearrangement of 1,4-Epoxy-1,4-dihydronaphthalene to Benz[*f*]oxepin[1]

Sir:

The photoisomerization of norbornadienes and 7-oxanorbornadienes to quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptanes (quadricyclanes) and the corresponding 7-oxaquadricyclanes appears to be general.[2] These reactions are thought to proceed through an excited state which possesses interaction between the formally unconjugated double bonds.[2b] We report at this time an analogous reaction, the conversion of 1,4-epoxy-1,4-dihydronaphthalene to benz[*f*]oxepin **3** in a photoisomerization that apparently goes by way of intermediate **2**.



1a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$

2

3a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$

Irradiation[3] of 1% solution of **1a**[4] in ether or absolute ethanol for 48 hr gave benz[*f*]oxepin **3a** in 4% yield or 6% in sealed, degassed tubes. The structure of **3a** was established by comparison of its melting point and infrared, ultraviolet, and nuclear magnetic resonance spectra with those reported by Dimroth, *et al.*[5] When the reaction was attempted in the presence of sensitizers,[6] no **3a** was formed. A small amount of a dimer was formed along with a large amount of other high molecular weight material. This suggests two conclusions. (1) The oxepin is formed from an excited singlet state of **1a**. (2) Direct excitation of **1a** does not lead to any significant yield of triplets.

In order to elucidate the mechanism of the transformation to benz[*f*]oxepin, **1b**[4] and **1c**[7] were synthesized and photoisomerized.

Figure 1 presents the vinyl regions of the nmr spectra for compounds **3a–c**.[8] It is expected that benz[*f*]oxepins are separated from their arene oxide valence tautomer by a relatively high energy barrier and that the nmr spectra are due only to the oxepin forms. If this is true, the anomalous shifts observed in the spectrum of

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(1) Mechanisms of Photochemical Reactions in Solution. LI. Part L: L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, in press.

(2) (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (d) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (e) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964); (f) P. G. Gassman, D. H. Ave, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (g) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (h) H. Tanick, Y. Hata, Y. Matsui, and J. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965); (i) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966); (j) E. Pazo, L. Cortés, J. Mantećon, C. Rivas, and G. de Pinto, *Tetrahedron Letters*, 2415 (1967); (k) H. Prinzbach, reported at the International Symposium on Photochemistry, Enschede, July 1967.

(3) A low-pressure Hg resonance lamp was used. About 90% of its intensity is at 2537 Å.

(4) E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961). Our material was prepared *via* benzyne generated from anthranilic acid by a variation of the method of L. Freidman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

(5) K. Dimroth, G. Pohl, and H. Follmann, *Ber.*, **99**, 634 (1966).

(6) Acetophenone, benzophenone, and acetone were tried as sensitizers.

(7) Furan-2,5-d_2 and benzyne gave **1c** in 70% yield. Furan-2,5-d_2 was prepared by metalation of furan with a threefold excess of *n*-BuLi in refluxing ether for 4 hr, followed by quenching with D_2O. The material was shown by nmr to be 80% dideuterated.

(8) Suitable carbon and hydrogen analyses were obtained for this compound (mp 44–45°). The nmr showed three regions: aromatic protons at τ 2.8–3.7, vinyl protons at τ 4.1–5.0, and methyl protons at τ 8.30 in the ratio 4:3:3. The infrared spectrum had strong peaks in the 1650 and 1050-cm^{-1} regions.

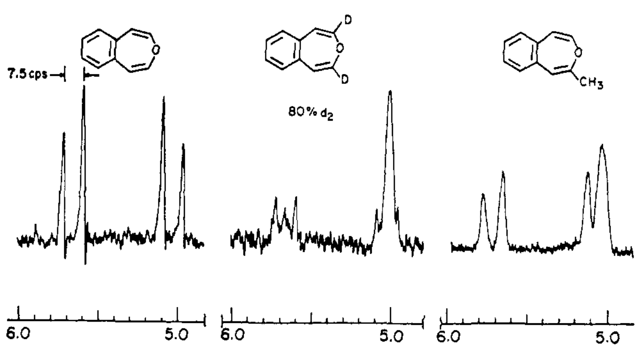

Figure 1. Nmr spectra of compounds **1a**, **1b**, and **1c** in deuteriochloroform; scale is parts per million downfield from internal tetramethylsilane.

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.

Acknowledgment. This work was supported by the National Science Foundation.

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[9] E. Vogel and H. Gunther, *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[11] National Institutes of Health Postdoctoral Fellow.

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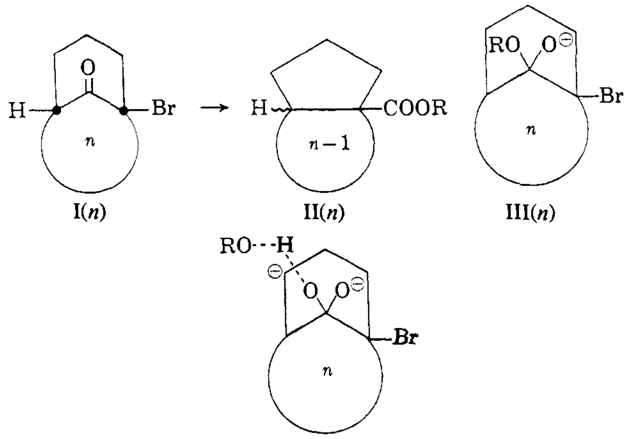
Mechanistic Changes in a Favorskii Reaction[1]

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-



I(*n*) II(*n*) III(*n*)

IV(*n*)

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

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[1] α-Halo Ketones. VI.

[2] R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

[3] B. Tchoubar and O. Sackur, *Compt. Rend.*, **208**, 1020 (1939).

[4] (a) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); (b) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960); (c) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961); (d) A. W. Fort, *ibid.*, **84**, 2620, 2625 (1962); (e) A. Gaudemer, J. Parello, A. Skrobek, and B. Tchoubar, *Bull. Soc. Chim. France*, 2405 (1963); (f) R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965); (g) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965); (h) R. Deghenghi, G. Schilling, and G. Papineau-Couture, *Can. J. Chem.*, **44**, 789 (1966); (i) A. Skrobek and B. Tchoubar, *Compt. Rend.*, **C263**, 80 (1966); (j) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966); (k) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967); (l) F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *ibid.*, **89**, 6704 (1967).

[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).

[7] Rearrangement of I(6) to II(6) was first reported by A. C. Cope, M. E. Synerholm, and E. S. Graham [*J. Am. Chem. Soc.*, **72**, 5228 (1950); **73**, 4702 (1951)], who suggested that the rearrangement probably proceeded by a semibenzilic path in view of the low acidity of the bridgehead α'-hydrogen atom.

[8] E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Org. Chem.*, **32**, 2664 (1967).