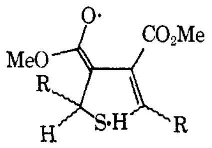
over that with the episulfide linkage at the alternate double bond; this follows from the similarities of the chemical shifts of the tertiary and vinylic protons to those for **8** and from the high degree of deshielding of the methylene group indicating it to be cis to carbomethoxy. Structure **5** is that expected for the precursor of **7** but is assigned only on that basis.

The stereoselectivity of the transformations of **1–3** is not accommodated readily by extant theory. Application of some of the Zimmerman postulates[9] to the n–π^* excited states of **1–3** does allow rationalization of the gross details of these unique ring contractions.[10] Biradical **13** would be a key intermediate and its formation finds precedent in the photoreactions of some structurally related isothiochromanones.[11] The chief products from the reactions of **1** and **3** may be accounted for by assuming a high preference for outward rotation of the alkyl group at the potentially vinylic carbon concomitant with nascent thiyl radical elimination;[12] readdition of the thiyl radical must then occur so as to arrange the alkyl and carbomethoxy groups trans on the episulfide ring. The pronounced tendency of cis isomer **2** to yield ultimate product **7** is more difficult to explain; also the irreversible isomerization of **1** to **2** (note Chart I) is puzzling. The alternative Woodward–Hoffmann theory[13] (assuming concerted reaction) encounters even more serious difficulties.[14] The transformations of **1** and **3** to **4** and **8**, respectively, are nominally $_\sigma 2_s + {}_\pi 2_s$ reactions with only one of two allowed products (episulfide linkage at alternate double bond) being formed.[15,16] Problems arise again with **2**, however. Ultimate product **7** could come from an allowed *supra–supra* reaction but the total absence of equally allowed ultimate product **12** seems inconsistent with prediction.[17]



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Consideration of molecular models suggests that conformational factors might complement the above arguments to a significant degree. Further work is in progress.

Acknowledgment. The expert assistance of Mrs. K. S. Rozema with CAT and decoupling experiments is acknowledged gratefully. Mr. J. Buter prepared a supply of **3**.

[9] H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

[10] (a) Structurally related 2,3,5,5-tetraphenyl-2,5-dihydrofuran undergoes photochemical ring opening concomitant with group migration: D. W. Boykin, Jr., and R. E. Lutz, *J. Amer. Chem. Soc.*, **86**, 5046 (1964); (b) butadiene sulfones lose SO_2 photochemically yielding primarily conrotatory diene products: J. Saltiel and L. Metts, *ibid.*, **89**, 2232 (1967). The thermal reaction is exclusively disrotatory: W. L. Mock, *ibid.*, **88**, 2857 (1966); S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966). Pyrolysis of the sulfones of **1** and **3** at 290° produces exclusively dienes **6** and **10** (disrotatory products).

[11] W. C. Lumma Jr., and G. A. Berchtold, *J. Org. Chem.*, **34**, 1566 (1969).

[12] Review of thiyl radicals: R. M. Kellogg, "Methods in Free-Radical Chemistry," E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, pp 1–120.

[13] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969).

[14] For trenchant criticism of the applicability of the Woodward–Hoffmann rules in photochemical reactions see: W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[15] But high preference for one of two "allowed" pathways in a photochemical rearrangement has been observed in other systems; see, for example: L. A. Paquette and O. Cox, *ibid.*, **89**, 5633 (1967); W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965).

[16] This transformation remains $2_s + 2_s$ even if, against probability, the position of the episulfide linkage is incorrectly assigned in **4** and **8**.

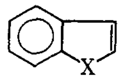
[17] The Woodward–Hoffmann theory does explain nicely the total absence of any *a priori* energetically favorable cycloreversion of **1–3** to thiocarbonyl ylide and acetylenic ester; the allowed *supra–antara* geometry for photochemical cycloreversion is unattainable preventing this reaction. A search of the literature on Δ^3-unsaturated sulfur containing five-membered heterocycles indicates that similar considerations may obtain in some strikingly dichotomous thermal and photochemical reactions. For example: (a) R. M. Kellogg and S. Wassenaar, *Tetrahedron Lett.*, 1987 (1970) [subsequently also reported by D. H. R. Barton and B. J. Willis, *Chem. Commun.*, 1225 (1970)] observed that Δ^3-1,3,4-thiadiazolines decompose thermally to N_2 and thiocarbonyl ylides and photochemically to azines and singlet sulfur (W. L. Prins and R. M. Kellogg, work in progress); (b) R. W. Hoffmann and H. J. Luthardt (*Chem. Ber.*, **101**, 3861 (1968)) observed that Δ^3-1,3,4-oxadiazolines thermally give N_2 and carbonyl ylides but photochemically give (likely) a carbene and diazo compound; (c) H. H. Inhoffen, R. Jonas, H. Kröshe, and U. Eder (*Justus Liebigs Ann. Chem.*, **694**, 19 (1966)) found that Δ^3-1,3,4-thiadiazoline 1,1-dioxides lose N_2 and SO_2 pyrolytically but give a ketazine and SO_2 photochemically.

Richard M. Kellogg
Department of Organic Chemistry, Zernikelaan
The University, Groningen, The Netherlands
Received January 15, 1971

The Isolation of Isobenzofuran, a Stable but Highly Reactive Molecule

Sir:

The series of π excessive heterocyclic compounds containing a single heteroatom and isoelectronic with naphthalene falls distinctly into two classes.[1] The parent compounds in the so-called "normal" series[2] (**1**: X = O; benzofuran; X = S, benzothiophene; and X = NH, indole) are well known and quite stable, whereas the isoconjugate isomers (**2**: X = O, isobenzofuran; X = S, isothianaphthalene; and X = NH, isoindole), with the exception of isothianaphthalene,[3] have resisted isolation although they are known as transient reaction intermediates.[4,5] Dewar and his coworkers[2] have recently reported the results of a series of calculations, employing the semiempirical SCF–MO π approximation method, which indicate that isobenzofuran is practically devoid of aromatic character (E_R = 2.4 kcal/mol)[6] and predict, on the basis



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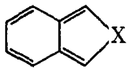

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[1] For a definition of π excessive, as well as work on the related 10π-azulene system, see A. G. Anderson, Jr., and D. M. Forkey, *J. Amer. Chem. Soc.*, **91**, 924 (1969).

[2] M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, *Tetrahedron*, **26**, 4505 (1970).

[3] (a) R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, 20, 244 (1963); (b) M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, **88**, 4112 (1966).

[4] Isobenzofuran: (a) L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965); (b) R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5231 (1969); (c) W. S. Wilson and R. N. Warrener, *ibid.*, 5203 (1970).

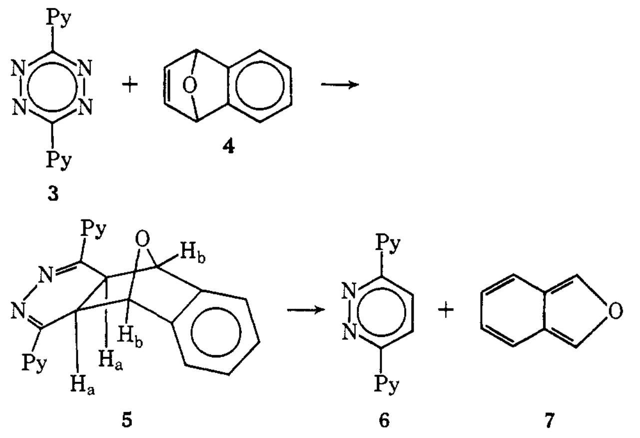
[5] Isoindole: R. Kreher and J. Seubert, *Z. Naturforsch. B*, 20, 75 (1965).

[6] These calculations predict that isoindole should be more stable (E_R = 11.6 kcal/mol); this may account for the increased stability of N-substituted isoindoles.[7] The parent compound, however, has only been isolated as its Diels–Alder adduct with maleic anhydride or *N*-phenylmaleimide.[5]

of the calculated CC bond lengths, that it should resemble the "polyene." Our results partly support this prediction although isobenzofuran now appears more stable than the related carbocyclic systems *o*-xylylene[8] and isoindene.[9]

Reaction of a suspension of 3,6-di(2′-pyridyl)-*s*-tetrazine (**3**)[12] with 1,4-dihydro-1,4-endoxynaphthalene (**4**)[4a] in dimethyl sulfoxide solution occurred rapidly at room temperature (exothermic, N_2 elimination) to precipitate the yellow dihydropyridazine derivative (**5**)[13] (Scheme I). This compound slowly decomposed on storage in the solid state, but was quite stable in solution below −20°. Decomposition was rapid at around room temperature and pmr spectroscopy indicated that quantitative conversion into the pyridazine (**6**) and isobenzofuran (**7**) had occurred.[14] Attempts to isolate the isobenzofuran from these solutions by conventional means were unsuccessful due to the rapid polymerization of the isobenzofuran, but its formation was confirmed by the addition of *N*-methylmaleimide which rapidly formed a mixture of the exo (**10**) and endo adducts (**11**) (see Figure 1).[16]

Scheme I



Py = 2-pyridyl

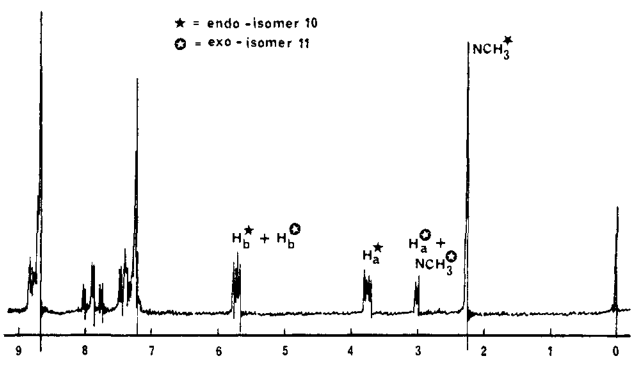
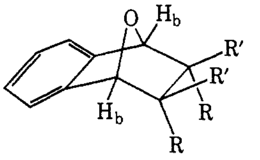


Figure 1. Pmr spectrum of the reaction mixture from decomposition (room temperature) of **5** in chloroform-*d* solution in the presence of *N*-methylmaleimide.

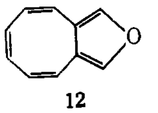
Figure 2. Pmr spectrum of isobenzofuran in DMSO-d_6.



9, R′ = R = CN

10, R′ = H_a; R—R = CON(CH_3)CO

11, R = H_a; R′–R′ = CON(CH_3)CO



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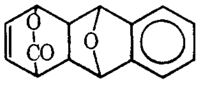
Pure crystalline isobenzofuran was readily obtained in high yield by controlled pyrolysis of **5** at 120° under reduced pressure (0.1 mm).[17] The volatile isobenzofuran was collected on a cold finger at −80°, as a colorless crystalline solid, mp *ca.* 20°; the nonvolatile pyridazine (**6**) remained in the pot. The isobenzofuran



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(7) *Inter alia* *N*-methylisoindole, mp 90–91°: G. Wittig, H. Tenhaeff, W. Schock, and G. Koenig, *Justus Liebigs Ann. Chem.*, **572**, 1 (1951).

(8) F. R. Farr and N. L. Bauld, *J. Amer. Chem. Soc.*, **92**, 6695 (1970), and references therein.

(9) Isoindene has only been isolated as its maleic anhydride adduct,[10] although it and its derivatives are commonly accepted intermediates in indene isomerizations.[11]

(10) J. A. Berson and G. B. Aspelin, *Tetrahedron*, 20, 2697 (1964).

(11) *Inter alia* J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 4316 (1970).

(12) J. F. Geldard and F. Lions, *J. Org. Chem.*, **30**, 318 (1965); W. S. Wilson and R. N. Warrener, *Tetrahedron Lett.*, 4787 (1970).

(13) Isolated yield 65%. No definite melting point. The main feature of the pmr spectrum is the lack of coupling between H_a (δ 3.69) and H_b (δ 5.80) which is consistent with the designated stereochemistry.

(14) In view of the reverse electron demand requirements of the *s*-tetrazine (**3**) in (4 + 2)π cycloadditions[4c] it is possible to carry out isobenzofuran cycloaddition at room temperature quantitatively in one step. Thus, equimolar amounts of **3**, **4**, and the dienophile are mixed together and solvent is added. Initial cycloaddition occurs with the 1,4-endoxynaphthalene whose dienophilicity is increased by ring strain, and further, by orbital participation of the n electrons of the proximate oxygen atom;[15] subsequent fragmentation liberates the isobenzofuran which in turn reacts with the classical electron-poor dienophile.

(15) An orbital-symmetry treatment of this phenomenon will be the subject of a future communication.

(16) The exo and endo adducts were readily distinguished by the coupling of the bridgehead methine protons; only the endo isomer showed the characteristic AA′BB′ quartet.

(17) A similar pyrolysis of **8** at its melting point also formed isobenzofuran, but this was only obtained in poor yield and contaminated with benzene. Much polymeric material remained in the pot.

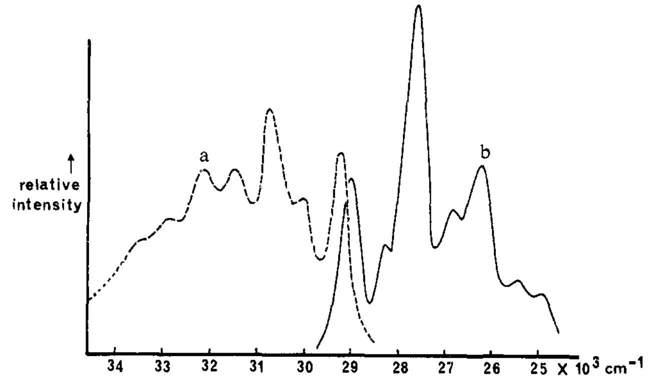

Figure 3. Electronic spectra of isobenzofuran: (a) absorption spectrum in hexane (broken line); (b) fluoresence spectrum at 77°K in isopentane–methylcyclohexane, 3:1 (solid line).

was characterized as its tetracyanoethylene adduct, **9**, mp 204°. The mass spectrum[18] of isobenzofuran showed a strong parent peak at *m/e* 118 (high resolution 118.04196; calcd for C_8H_6O, 118.04186) as well as major peaks at *m/e* 90 (P − CO, m* 68.6) and *m/e* 89 (90 − H, m* 88.2). The pmr spectrum (Figure 2) clearly supports the isobenzofuran structure, in which the downfield singlet is assigned to the furanoid protons. The pronounced downfield shift of these resonances (δ 8.40) compared with those found in cycloocta[*c*]furan (**12**) (δ 7.20),[19] implies the presence of a strong diamagnetic ring current, typical of other aromatic 10π planar systems.[20] The ultraviolet absorption spectrum (Figure 3) is very similar to that reported for isothianaphthalene.[3a] The lack of solvent dependence on the position of this absorption band, together with the mirror relationship of the fluorescence spectrum,[21] support the $\pi \rightarrow \pi^*$ character of the lowest singlet transition, which is again consistent with the oxygen n electrons being involved in the overall 10π system. It is not possible at this time to comment further on the significance of these results in terms of the aromaticity of isobenzofuran, particularly in view of the lack of model carbocyclic systems.

Acknowledgment. We thank the Australian Research Grants Committee for partial support of this work.

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[18] We thank Dr. J. MacLeod and Mr. K. Goggin for the mass spectra (recorded on an AEI MS902 instrument, operated at 70 eV).

[19] E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965).

[20] G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, 1969, p 61.

[21] We thank Dr. B. K. Selinger and Mr. R. J. McDonald of this department for this measurement. For a description of the apparatus used see R. J. McDonald and B. K. Selinger, *Z. Phys. Chem. (Frankfurt am Main)*, **69**, 132 (1970).

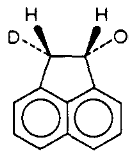
Ronald N. Warrener
Department of Chemistry, School of General Studies
Australian National University, Canberra, A.C.T. 2600, Australia

Received March 2, 1971

E1cB Reactions. Stereochemistry and the Counterion

Sir:

We wish to report observations on base-catalyzed elimination reactions of 1-methoxyacenaphthenes which appear to proceed with reversible formation of carbanionic intermediates.[1] Under the present conditions, elimination and hydrogen–deuterium exchange reactions were in close competition, and allowed observation of the stereochemical preferences of both processes. Both the elimination and exchange reactions changed from exclusive cis to preferential trans[2] stereoselectivity depending upon the nature of the cation in solution.



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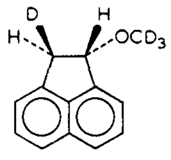

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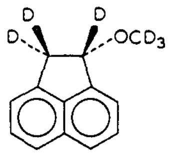

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cis-1-Methoxy-d_3-2-deuterioacenaphthene (**1**) and *trans*-1-methoxy-d_3-2-deuterioacenaphthene (**2**)[3] (0.01–0.06 *M*) were treated in degassed sealed tubes as in Table I. The products of reaction were analyzed by vpc and mass and nmr spectrometry. For each set of conditions three reactions were run (10, 30, and 50% elimination) but only a representative run is included for each. While the recovered ethers were also analyzed for exchange, these results have been omitted for simplicity; exchange occurs predominantly at the 2 position.[4]

The reactions of **1** and **2** were used to deduce the stereoselectivity of the elimination reactions. Analysis of the recovered acenaphthylenes allowed calculation of the amounts of acenaphthylene-d_0, -d_1, and -d_2[5] (see Table I). It is clear that the ratio of d_0 to d_1 varies widely and for discussion these results have been converted to $k_{\text{cis}}/k_{\text{trans}}$ elimination ratios in Table II. The conversion of the d_0/d_1 ratio to $k_{\text{cis}}/k_{\text{trans}}$ elimination involved extrapolation to zero time and the ratios changed by about 10% on extrapolation. Also included in Table II under the heading $k_{\text{cis}}/k_{\text{trans}}$ exchange are exchange results for 1-methoxy-d_3-1,2,2-trideuterioacenaphthene (**3**).[4]

In Table II under the heading ex/elim is a comparison of the relative amounts of total exchange of the ether and elimination based upon these and earlier results.[4] Comparison of the rates of elimination of **3** and of 1-methoxyacenaphthene yielded kinetic isotope effects for the reactions in *tert*-butyl alcohol with Cs^+, K^+, and K^+-crown ether[6] as cations. These fall in the range k_H/k_D = 1.6–1.8.[7] The observation of hydrogen–deuterium exchange requires the formation of carbanionic intermediates for the exchange reaction; it seems

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[1] For a recent discussion of types of E1cB reactions see F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5950 (1970).

[2] The terms cis and trans (rather than syn or anti) will be used throughout to designate the geometrical relationship of the proton (deuteron) to the methoxy group in both the exchange and elimination processes.

[3] Ether **1** was prepared *via* the alcohol from deuterioboration of acenaphthylene; ether **2** was prepared *via* the alcohol from $LiAlD_4$ reduction of 1,2-epoxyacenaphthene. Both ethers were $\geq$99% chemically pure and about 90% isotopically pure.

[4] D. H. Hunter and Y. T. Lin, *ibid.*, **90**, 5921 (1968).

[5] Acenaphthylene-d_2 exchange approximately 10^7 slower than **3**.

[6] (a) Dicyclohexyl-18-crown-6-ether kindly provided by H. K. Frensdorff, E. I. du Pont de Nemours and Co., Wilmington, Del.; (b) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

[7] (a) *E.g.* D. J. McLennan, *Quart. Rev., Chem. Soc.*, **21**, 490 (1967); (b) R. Breslow, *Tetrahedron Lett.*, 399 (1964); (c) H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, **92**, 2445 (1970); (d) W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 4661 (1967).