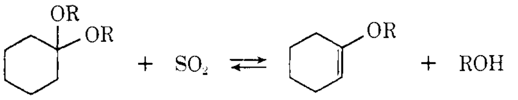
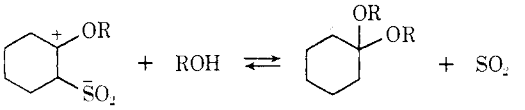


(5)

signal for the vinyl proton was observed, it would appear that the enol ether reacts with sulfur dioxide to form the 1,3-dipolar ion II (eq 1),[9] which is thus in equilibrium with the acetal (eq 6).



(6)

Because the charges in the 1,3-dipolar ion II are separated by an sp^3 hybridized carbon atom, their internal stabilization is not possible.[10] Nevertheless, the necessary stabilization may effectively be achieved through appropriate delocalization of charges over the oxygen atoms attached to positively charged carbon and negative sulfur. Contrary to a generally recognized contention that it is meaningless to assign an electrophilic and nucleophilic end to an internally stabilized 1,3 dipole,[11] such a dipolar ion as II does possess nucleophilic and electrophilic ends, and consequently it should react with appropriate dipolarophiles with predictable orientation. While the cycloadditions of internally stabilized 1,3-dipolar ions are symmetry allowed, concerted, suprafacial processes $({}_{\pi}4_s + {}_{\pi}2_s)$,[12] the cycloaddition of II to 1-alkoxycyclohexene (eq 2) obviously cannot proceed through the same process. Clearly, the flow of four π electrons between the charges which is possible in "regular" 1,3 dipoles of heteroallyl type[10] is not possible in II.

Both isomeric 3-alkoxy-1,3- and -1,4-dienes VA and VB react with sulfur dioxide to give the same product IV (eq 4). This sugests that the 1,4 isomer under reaction conditions isomerizes to the 3-alkoxy-1,3-diene (probably through the intermediate formation of the corresponding 1,3-dipolar ion), which then apparently reacts with sulfur dioxide in the usual manner[1] to give IV. Since it has been shown that sulfur dioxide–1,3-diene adducts lose sulfur dioxide in the concerted suprafacial mode,[13] it seems logical to assume that the cycloaddition reaction itself is also a concerted suprafacial process. On this basis one would assume that in IV, which was formed in a cycloaddition reaction of sulfur dioxide and VA, the hydrogen and alkoxy group α to the sulfone group are cis with respect to each other. Since the same product is also obtained by reaction of sulfur dioxide with 1-alkoxycyclohexene (eq 1–3), formation of III, albeit as a relatively unstable product, must also be a highly stereospecific reaction. However, the exclusive formation of a single product in this reaction should not be taken as evidence for concerted formation of the two new σ bonds in a $({}_{\pi}4_s + {}_{\pi}2_s)$ process. Observed stereospecificity may simply reflect the favored stereochemical arrangement in the transition state leading to III.

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[9] An alternative explanation that thus generated enol ether undergoes proton-catalyzed dimerization to 3-alkoxy-1,3- and -1,4-dienes V,[5] which is then removed from the system through reaction with sulfur dioxide, is inconsistent with the observed spectra. The absence of "free" ethanol in the reaction of the 1-alkoxycyclohexene itself with sulfur dioxide also seems to rule out this possibility.

[10] (a) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); (b) R. Huisgen, *ibid.*, **7**, 321 (1968).

[11] R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

[12] (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192, 2212 (1967).

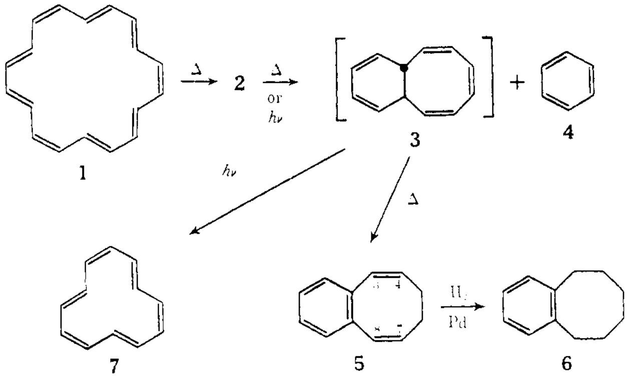
[13] (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

The Thermolysis of [18]Annulene[1]

Sir:

Although the nonaromatic [10]-, [12]-, and [16]-annulenes undergo ready thermal valence isomerization in solution to polycyclic isomers at room temperature or below,[2] it has previously not been possible to bring about similar reactions with the other known annulenes.[3] We now report the results obtained on heating solutions of the aromatic [18]annulene (**1**),[2] which surprisingly caused cleavage of the molecules to benzene (**4**)[4] and 1,2-benzo-1,3,7-cyclooctatriene (**5**). Furthermore, irradiation of an intermediate in this reaction has resulted in a new synthesis of [12]annulene (**7**).

[18]Annulene (**1**) in dry dimethylformamide (bp 163°) was boiled under reflux in nitrogen for 80 min. Chromatography on silica gel gave 63% of **5** as a colorless liquid: *m/e* 156; nmr spectrum (CCl$_4$, 60 MHz) τ 2.95 (s, 4 H, benzenoid), 3.53 (d, J = 12 Hz, 2 H, H^3, H^8), 3.9–4.4 (m, 2 H, H^4, H^7), 7.6–7.8 (m, 4 H, methylene). Structure **5** follows from these spectral data, as well as from the correspondence of the uv and ir spectra with those reported.[6] Further proof of identity was provided by preparation of the silver nitrate complex (mp 164–166° dec; reported mp 163–165° dec[6]) and by catalytic hydrogenation in cyclohexane over 5% Pd/



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[1] Unsaturated Macrocyclic Compounds. XCV. For part XCIV, see P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Lett.*, 3695 (1972).

[2] For references, see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

[3] [24]Annulene appears to be converted into a polycyclic isomer on standing in solution, but this reaction has not been investigated in detail (F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Amer. Chem. Soc.*, **84**, 274 (1962)).

[4] The cleavage of benzene was also observed to occur from 1,2-difluoro- and 1-chloro-2-fluoro[18]annulene,[5] in tetrahydrofuran at 80° and above, in the course of nmr studies (G. Schröder and J. F. M. Oth, unpublished observations).

[5] G. Schröder, R. Neuberg, and J. F. M. Oth, *Angew. Chem.*, **84**, 36 (1972).

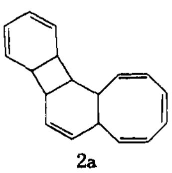
[6] G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).

CaCO$_3$ to 1,2-benzo-1-cyclooctene (**6**), identified by direct comparison with an authentic sample.[7] The formation of benzene in this experiment was shown by glc of the dimethylformamide solution, the estimated yield being $\sim$70%. Only trace amounts of other nonpolymeric products were obtained. The same substances **4** and **5** were formed when [18]annulene was boiled in diglyme (bp 161°) for 80 min.

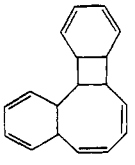
In order to discover intermediates in the conversion of **1** to **4** and **5**, the thermolysis of **1** in tetrahydrofuran-d_8 at various temperatures was monitored by nmr spectrometry. This showed that an intermediate was indeed formed after several hours at 90°, although its further transformation to **4** and **5** appeared to proceed at a rate comparable to its formation. In a preparative experiment, **1** in tetrahydrofuran was heated at 90° (sealed tube) for 9 hr, when the intermediate **2** could be isolated in $\sim$5% yield as an apparently homogeneous colorless liquid [λ_{max} (cyclohexane) 268 nm (ϵ 5600)] by preparative layer chromatography on silica gel, together with $\sim$75% of recovered **1**.[8]

The intermediate **2** was isomeric with [18]annulene, as shown by the mass spectrum at 25 eV (*m/e* 234).[9] Heating **2** in dimethylformamide at 130° for 11 hr led to its complete conversion to **4** and **5**, while photolysis in tetrahydrofuran-d_8 at $-100°$ for 10 hr with four low-pressure Hg lamps gave **4** and [12]annulene (**7**),[10] identified by its typical nmr spectrum (τ 3.04 (s), 3.98 (s), ratio 1:1, at $-115°$), and its known transformations on heating above $-40°$.[10,11] Hydrogenation of **2** in benzene over Pt, followed by glc, gave two saturated hydrocarbons in a ratio of $\sim$4:1, the mass spectra of which (*m/e* 246) showed them to be tetracyclic. This indicates that **2** is also tetracyclic, and this is in accord with the nmr spectrum (CDCl$_3$, 100 MHz) which showed multiplets at τ 3.85–4.55 (olefinic) and 6.40–7.95 (allylic) in a ratio of 2:1.

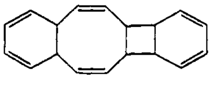
The three tetracyclic structures **2a**, **2b**, and **2c** are



2a



2b



2c

consistent with the above data, the ready thermal and photochemical elimination of benzene from such systems having precedent.[10,11] It has not been possible to distinguish between these structures, and the hydrogenation results suggest that **2** is probably a mixture of isomers.

The thermolysis of **2** to **5** and its photolysis to **7** presumably involve *trans*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**3**)[10,11] as an intermediate, which must have the indicated stereochemistry since the corresponding cis isomer is known to give only benzene on thermolysis[10,11] (the thermolysis of **3** has not been studied previously; the photolysis of either **3** or the corresponding cis isomer at $-100°$ is known to give [12]annulene[10]). The fusion between the eight- and the six-membered rings in **2** is therefore also trans.

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[7] Authentic **6** was obtained by catalytic hydrogenation of benzocyclooctatetraene, kindly provided by Mr. C. M. Bowes.

[8] Heating for more than 9 hr did not appreciably increase the yield of **2**, but resulted in larger amounts of **5** from which it was difficult to separate.

[9] The apparent molecular ion at 70 eV was at *m/e* 156, due to the ready elimination of benzene.

[10] J. F. M. Oth, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 61 (1970).

[11] H. Röttele, W. Martin, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **102**, 3985 (1969).

The Additive Nature of Group Enthalpies of Transfer from Methanol to *N,N*-Dimethylformamide

Sir:

Enthalpies of transfer ($\Delta\Delta H_s$) of ions and nonelectrolytes from protonic solvents such as water or methanol to dipolar aprotic solvents such as dimethyl sulfoxide or dimethylformamide have recently been of interest to several investigators[1-5] in studying the role of solvents in certain anionic displacement reactions. These quantities ($\Delta\Delta H_s$) are involved in determining the enthalpy of transfer of the transition state ($\Delta\Delta H^t$) from one solvent to another through the expression

$$\Delta\Delta H^t = \Delta\Delta H_s + \Delta\Delta H^{\ddagger}$$

where $\Delta\Delta H^{\ddagger}$ is the difference in enthalpy of activation of the reaction in the two solvents.

Only a few enthalpies of transfer of nonelectrolytes have been reported[2-5] and no trends have been noted among the available data.[1a]

We have determined $\Delta\Delta H_s$ values from methanol (MeOH) to *N,N*-dimethylformamide (DMF) for a series of aromatic compounds and some of their nitro and chloro derivatives and wish to report evidence of a unique *additivity* of enthalpies of transfer for the phenyl, nitro, chloro, and acetyl substituents. Preliminary results indicate that an additive relationship also exists in aromatic compounds containing fluoro, bromo, iodo, and carbethoxy groups and in saturated compounds including alkanes, alkyl halides, and nitroalkanes. The aliphatic group values differ somewhat from the aromatic. Enthalpies of solution (ΔH_s) and enthalpies of transfer (both observed and calculated) are reported in Table I. A negative $\Delta\Delta H_s$ value indicates increased solvation in the transfer from MeOH to DMF.

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[1] (a) H. L. Friedman, *J. Phys. Chem.*, **71**, 1723 (1967); (b) C. V. Krishnan and H. L. Friedman, *ibid.*, **73**, 3934 (1969); (c) *ibid.*, **74**, 3900 (1970).

[2] P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, **36**, 1792 (1971).

[3] P. Haberfield, L. Clayman, and J. S. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 (1969).

[4] E. M. Arnett and D. R. McKelvey, *ibid.*, **88**, 2598 (1966).

[5] R. Fuchs and L. L. Cole, manuscript submitted to *J. Amer. Chem. Soc.*