The dependence of structure B on the nature of R is probably not due to steric considerations since the greater size of the organometallic groups should result in a decrease of ΔG_a.[2] The percentage contribution of structure C, however, could be affected by the nature of R. For example, the organometallic groups may produce a smaller contribution because of possible (p–d) π bonding from Y to Si or Sn. A decrease in contribution of C would result in an increase in percentage contribution of form B (the percentage contribution of forms A and C could of course change in such a way as to keep their total contribution the same, but this seems less likely).

The percentage contribution of B for those compounds in which X = S is also greater than or equal to the contribution in compounds for which X = O, at least partially because of less effective π overlap between C and S, *i.e.*, smaller (or equal) contribution of structure A when X = S. When X = S, the contribution of resonance structure C apparently increases in going from Y = O to Y = S, presumably due to the greater ability of sulfur to stabilize the positive charge. When X = O, however, a variation of Y from O to S results in little change in the significance of C and thus little change in the contribution of structure B. The insensitivity of form C to a change of Y when X = O (relative to the compounds in which X = S) can be explained by assuming that the greater electronegativity of oxygen causes the C_π orbital to become energetically less compatible with the S_π orbital, thereby making the percentage contribution of form C roughly equal for Y = O and Y = S.

Acknowledgments. The authors are indebted to R. D. Schubert and W. S. Morris for their assistance in some of the synthetic aspects of this work.

Thermal Interconversion of Some (2 + 2) and (2 + 4) Adducts of Cyclopentadiene and Dichloroethylenes. Determination of Erythro and Threo Configurations

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Abstract: The C–C bond first formed in the photosensitized biradical cycloaddition of 1,2-dichloroethylene or 1,2-dichloro-1,2-difluoroethylene to cyclopentadiene remains unbroken during thermal rearrangements of the adducts at 400°. Thus only products of the same biradical (erythro or threo) are interconverted, and this makes it possible to complete the assignment of configurations to the bicyclo[3.2.0]heptene adducts. At this temperature the concerted sigmatropic mechanism is overshadowed by stepwise rearrangement *via* biradicals, and by decomposition.

In studies of thermal and photosensitized cycloaddition, the seven possible cycloadducts of 1,2-dichloroethylene[1] and of 1,2-dichloro-1,2-difluoroethylene[2] ("1212") to cyclopentadiene have been isolated and characterized. Evidence for the structures and configurations of these products is unambiguous except for pairs of *trans*-6,7-dichlorobicyclo[3.2.0]heptenes (**1H**, **2H**, **1F**, and **2F**, Scheme I). **1H** and **2H** were called VIIa and VIIb in ref 1, and **1F** and **2F** were called **3** and **4** in ref 2,[3] in each case without final assignment.

If, as there is good reason to believe,[1,2,4] the photosensitized cycloaddition proceeds by way of biradicals, then the cycloadducts are formed in two stereochemical families according to the relative configurations of the two asymmetric centers in the original biradical (**8** and **9**, Scheme I). Except for the trans (1,4) adduct **5**, which is a common product of both series, each product can arise from only one biradical, and may be designated as belonging to the erythro or to the threo series.[5]

If any biradical were to be re-formed from one of the (1,2) cycloadducts it should be, with overwhelming probability, the same biradical from which the adduct was originally formed, for only so can the stabilization belonging to an allylic cyclopentenyl radical and an α-chloroalkyl radical be attained. Because the only remaining question of structural assignment in these

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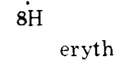
[1] P. D. Bartlett, R. Helgesson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968).

[2] R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 3822 (1970).

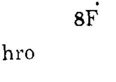
[3] VIIa and VIIb are characterized[1] by their yields at 25° when formed by α-acetonaphthone photosensitization from *cis*- and *trans*-dichloroethylenes, respectively. VIIa: 49.4 and 20.9%; VIIb: 13.6 and 17.4%. VIIa is eluted before VIIb in the vpc separation. 3 and 4[2] are formed from *cis*- and *trans*-1212, respectively, in the following yields: thermal, 3, 0.9 and 1.2%; 4, 1% in each case; photosensitized, 3, 11.5 and 15.7%; 4, 40.0 and 25.2%. 3 (ref 2) is eluted before 4 (ref 2) in the vpc separation.

[4] P. D. Bartlett, *Science*, **159**, 833 (1968).

[5] Erythro and threo designations are defined by regarding the "free radical" carbon atoms on the two asymmetric centers as corresponding groups, and considering that F corresponds to H in the 1,2-dichloro-1,2-difluoroethylene series:

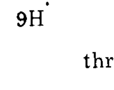


8H

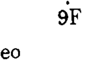


8F

erythro



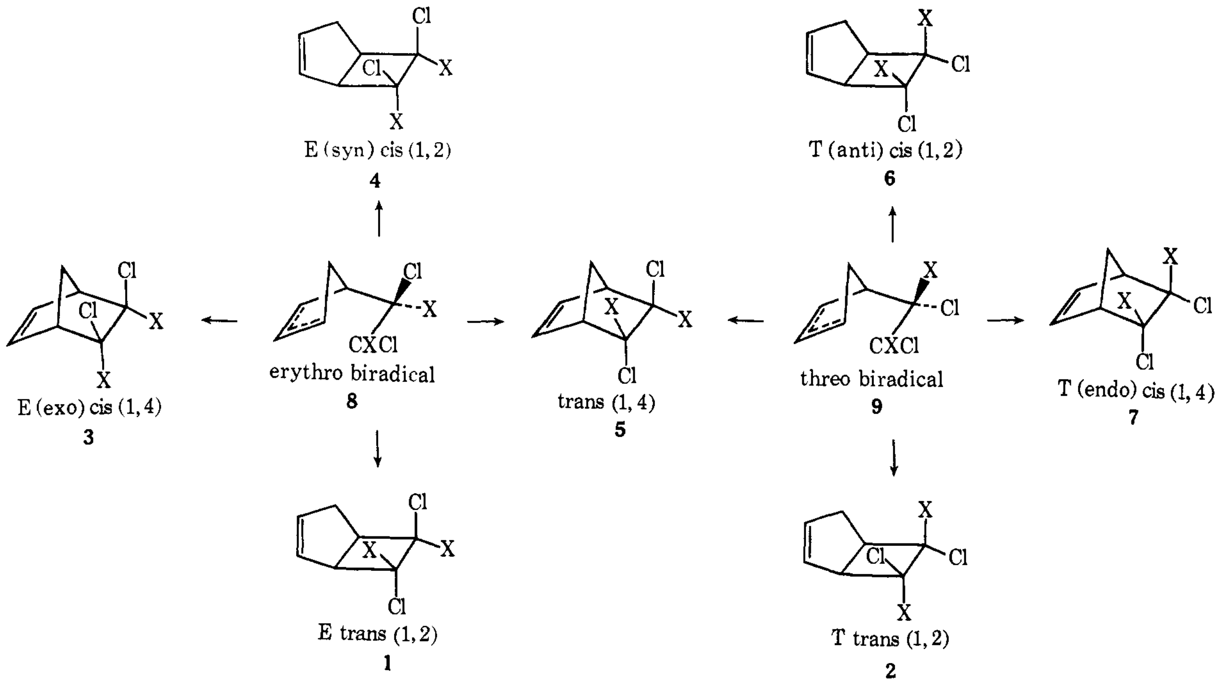
9H



9F

threo

Scheme I. Erythro and Threo Families of Cycloadducts of CXCl=CXCl to Cyclopentadiene (X = H or F)



two series was between the erythro-trans (1,2) and threo-trans (1,2) configurations, **1** and **2**, we have investigated the mixtures into which the compounds in question are converted on rapid pyrolysis.

Experimental Section

In the series of 1,2-dichloroethylene cycloadducts to cyclopentadiene four of the compounds were isolated and purified by vapor phase chromatography. These compounds were the endo-cis (1,4) (**7H**) and the anti-cis (1,2) (**6H**), both of known structure and belonging to the threo family, and the two trans (1,2) adducts (previously called VIIa and VIIb[1]) whose configurations were to be determined, one being erythro (**1H**) and the other threo (**2H**). They were purified through a column of Carbowax 20 M (20% on Chromosorb P), 30 ft × 0.375 in., maintained at 150° on a Varian Autoprep instrument. Each compound was shown to be more than 99% pure by analytical chromatography on a 30 ft × 0.25 in. column under the same conditions on an F & M 609 vapor chromatograph equipped with a flame ionization detector. A small sample of **7H** was further recrystallized from *n*-hexane.

In the case of the dichloroethylene adducts 40–60-mg samples were passed in a helium stream through a section of aluminum tubing packed loosely with glass wool and maintained at 400 ± 10° in the oven of the Autoprep instrument, the injection and detection blocks being maintained at 200°, and the helium stream adjusted so that the residence time in the 400° section was about 1 sec. The brown liquid recovered from such a pass, and representing about a 75–80% recovery, was injected in small samples into the analytical instrument for product assay. A mixture of the thermal and photosensitized cycloadducts (**1H–7H**) of cyclopentadiene and dichloroethylene, showing all seven possible components, was frequently sampled during these experiments to maintain a constant check on the retention times of the products.

In the 1,2-dichloro-1,2-difluoroethylene series the cis (1,4) thermal adduct **3F**, with the chlorine atoms exo, was purified on an Aerograph Autoprep vapor chromatograph at 170° with a 10 m × 1/4 in. column of 20% Carbowax 20 M on acid-washed 30–60 Chromosorb W treated with dimethyldichlorosilane. In a second purification (50-μl injection) only about two-thirds of the peak was collected. Such material showed no impurities on rechromatography. The pyrolysis was carried out as with the other four compounds, the rate of helium flow being varied to control the extent of conversion so that the identified cycloadducts amounted to at least ten times the detection limit.

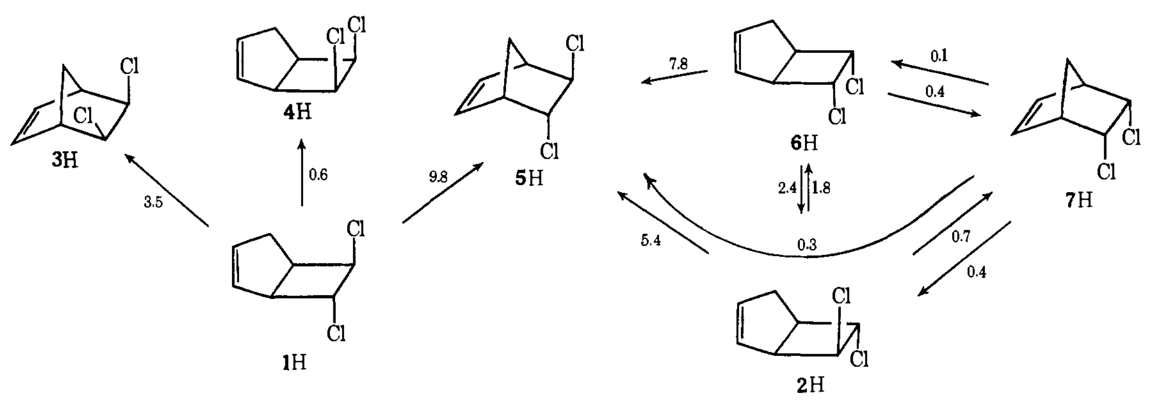
Results

The retention times of the dichloroethylene cycloadducts (**1H–7H**) under the conditions of these analyses cover the range from 7.7 min for trans (1,4) (**5H**) to 25.5 min for erythro (syn)-cis (1,2) (**4H**). In addition to the cycloadducts, each of which was observed in at least one pyrolysate, six unknown products were also observed. These unknowns, however, did not obscure any of the peaks due to the known cycloadducts, and

Table I. Pyrolysis Product Compositions of 1,2-Dichloroethylene–Cyclopentadiene Cycloadducts at 400°

Compd pyrolyzed	Retention time, min	Product	%
VIIa of ref 1	6.4	A	0.3
	7.7	5H, trans (1,4)	9.8
	8.3	VIIa	57.3
	10.2	B	0.2
	11.4	C	2.5
	12.2	D	15.1
	14.3	E	8.9
	14.7	3H, erythro (exo)-cis (1,4)	3.5
	17.3	F	1.6
	25.5	4H, erythro (syn)-cis (1,2)	0.6
VIIb of ref 1	6.4	A	0.2
	7.7	5H, trans (1,4)	5.4
	9.1	VIIb	89.8
	11.5	C	0.5
	12.2	D	1.0
	13.1	6H, threo (anti)-cis (1,2)	1.8
	14.3	E	0.6
	21.0	7H, threo (endo)-cis (1,4)	0.7
6H, threo (anti)-cis (1,2)	6.2	A	0.2
	7.7	5H, trans (1,4)	7.8
	9.0	VIIb	2.4
	11.3	C	1.2
	13.0	6H, threo (anti)-cis (1,2)	87.9
	19.8	7H, threo (endo)-cis (1,4)	0.4
7H, threo (endo)-cis (1,4)	7.7	5H, trans (1,4)	0.3
	9.0	VIIb	0.4
	11.3	C	0.2
	12.1	D	0.4
	13.0	6H, threo (anti)-cis (1,2)	0.1
	14.1	E	0.1
	21.0	7H, threo (endo)-cis (1,4)	98.4

Scheme II. Thermal Interconversions of the Cycloadducts of 1,2-Dichloroethylene to Cyclopentadiene in a Helium Stream at 400°



the most important observations in these experiments were the voids where particular compounds would have appeared if present. Most of the compounds gave pyrolysis products in which the converted portion consisted about half of unknowns and half of mixtures of certain of the known isomers. Table I lists the semiquantitative compositions of the product mixtures arrived at by multiplying attenuations and peak heights and widths at half height, and Scheme II indicates, with figures by the arrows, all the products obtained from each isomer and their relative amounts. In the table the known isomers are recognized by direct comparison of retention times in known mixtures. In the table the unknowns are assigned letters.

The compositions shown in Table II are the averages of two integrations with a Hewlett-Packard Model 3370A digital integrator in conjunction with an F & M Scientific Model 7620A research chromatograph in the flame mode. In both series of compounds it is assumed that the response factors of the detector to the several isomers are the same.

Table II. Pyrolysis Product Composition of *erythro-(exo)-cis*-5,6-Dichloro-*endo*-5,6-difluoronorbornene at 400°

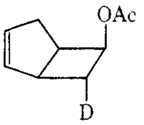
Retention time, min	Product	% with helium flow rate cm³/min 400	48	15
58	4 of ref 2	0.04	0.3	0.9
61	4F, erythro (syn)-cis (1,2)	0.05	0.7	1.5
63	5F, trans (1,4)	2.1	3.8	4.5
68	3F, erythro (exo)-cis (1,4)	97.8	95.2	93.0

Not surprisingly, the trans (1,4) isomer **5** in each series is a favored product of the thermal reaction at 400°. This fact alone is uninformative, since this is the one isomer which can be produced from biradicals of both the erythro and the threo configuration. Examination of the array of other known products in Tables I and II and Scheme II shows clearly that the erythro or threo character is maintained during the rearrangements and therefore, as demonstrated previously for rearrangements of bicyclo[3.2.0]- to bicyclo[2.2.1]heptenes,[6,7] the C_5–C_6 bond must remain intact during the process. Regardless of any assumption about the concerted or stepwise nature of the rearrangement, then, Table I shows emphatically that the trans (1,2) adduct designated previously[1,3] as VIIa belongs to the erythro series and is **1H**, while VIIb belongs to the threo series and is **2H**. Similarly, Table II establishes that the 1,2-dichloro-1,2-difluoroethylene (1212) adduct previously[2,3] called **4** has the erythro configuration **1F**, and its companion[2] **3** is in the threo family and is **2F**.

Discussion

Although the bicyclo[2.2.1]heptenes are favored thermodynamically over the bicyclo[3.2.0]heptenes, the present results show that at 400° there is interconversion in both directions. Therefore the success of this method of establishment of configuration depends not only upon the absence of cycloreversion and readdition,[6,7] but upon keeping the conversion low enough so that the erythro and threo series are not interconverted through their common member, the trans (1,4) adduct **5**. Despite the sensitivity of the detection system, which is capable of detecting as little as 0.1% of a product, no conversion of one series into the other was noted even in the reaction of VIIa in which trans (1,4) (**5H**) represented 9.8% of the product. This is perhaps due both to the superior stability of trans (1,4) and to the short time during which the stream was exposed to the high temperature, minimizing secondary reactions.

At 306° *endo*-6-acetoxybicyclo[3.2.0]hept-2-ene-7-*exo*-*d* (**10**) rearranges to *exo*-5-acetoxynorbornene-*exo*-6-*d* (**11**) with not more than 3–5% retention of configuration at the migrating CHD group.[8] The mechanism at 306° is accordingly a concerted 1,3-sigmatropic rearrangement with configurative inversion at the migrating center as required by the orbital symmetry rules.[9] Allowing for the possibility that as much as 3–5% of the rearrangement occurred by a nonstereospecific biradical path, Berson has estimated that this path might lead over a transition state 2.5 kal/mol higher in free energy than that of the concerted path,[10] and that any change to substituents more bulky than hydrogen might alter this differential to favor the step-



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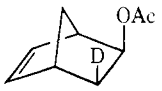

11

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[6] J. A. Berson and J. W. Patton, *J. Amer. Chem. Soc.*, **84**, 3406 (1962).

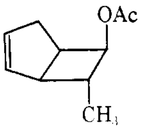
[7] J. A. Berson and R. S. Wood, *ibid.*, **89**, 1043 (1967).

[8] J. A. Berson and G. L. Nelson, *ibid.*, **89**, 5503 (1967).

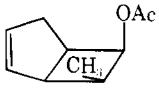
[9] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 827 (1969).

[10] J. A. Berson, *Accounts Chem. Res.*, **1**, 159 (1969).

wise path. Berson and Nelson[11] have found an example in the comparison of **12**, which at 290° rearranges



12



13

with at least 91% inversion, with **13**, in which inversion represents as little as 1.4% of a product mixture suggestive of biradical intermediates. It is therefore of interest to examine the incidental information which our experiments provide concerning the stereochemical course of the rearrangement when the migrating group is the CHCl or CFCl group, and the temperature 100° higher than in Berson's cases.

Table III shows that among the cycloadducts of 1,2-dichloroethylene to cyclopentadiene the cis isomers rearrange with predominant inversion (greater for (1,2) → (1,4) than for (1,4) → (1,2)) but that the trans isomers rearrange with predominant retention. In the one case of a difluorodichloroethylene cycloadduct there is more retention than inversion even though the rearranging compound is a *cis*-norbornene (**3F**).

Table III. Stereochemical Course of the Rearrangements of Tables I and II

Compound pyrolyzed	Inversion/retention on isomerization
H Series	
Erythro-trans (1,2), 1H	0.36
Threo-trans (1,2), 2H	0.12
Threo (anti)-cis (1,2), 6H	19.5
Threo (endo)-cis (1,4), 7H	4.0
F Series	
Erythro (exo)-cis (1,4), 3F	0.6

It should be emphasized that the observed restriction of the rearrangements to the configurative family, erythro or threo, of the starting material completely eliminates a cycloreversion–cycloaddition mechanism for the isomerizations. The mixture of retention and inversion of configuration at the migrating group therefore means either that the rearrangements in the present case are entirely *via* biradicals and nonstereospecific, or that biradical and concerted sigmatropic mechanisms are competing. The fact that each of the four products in the dichloroethylene series contains more trans than cis isomers does not of itself distinguish between these possibilities. More information is had by a direct comparison of the trans:cis ratio in the products, **5H**:**7H**, obtained from **6H**, which should yield the biradical **9H** in an initial phase of rotation having the chlorines cis, and from **2H**, which should yield the same biradical in a trans (Cl, Cl) conformation. In any pure biradical mechanism the trans/cis product ratio should either be the same from **6H** and **2H**, or should show incomplete rotational equilibration by the products showing some excess of the original configuration. Actually the ratio **5H**:**7H** is 19.5 from the cis isomer **6H**, but 7.7 from the trans isomer **2H**, indicating inversion beyond the point of rotational equilibration.

These figures allow some limiting conclusions. (1) In the extreme case in which all biradical rearrangement proceeds with retention (an unknown situation in model cases), **2H** would be rearranging with 11.5% concerted inversion mechanism and its cis isomer **6H** would be reacting 95% in the concerted manner. Such a low proportion of biradical mechanism as 5% in **6H** is actually ruled out by the fact that the direct conversion of **6H** to **2H** (possible only by a biradical process) amounts to 23% of its total isomerization.

In another extreme case it might be assumed that **2H**, the isomer with the greater hindrance in the concerted inversion mechanism, is rearranging entirely by way of a biradical which comes to rotational equilibrium. In this case the concerted mechanism could represent as little as 57% from **6H** and zero from **2H**. The fraction of concerted mechanism favored for **12** at 290° by Berson and Nelson [ref 11, footnote 9] falls near our upper limit for the analogous **6H**.

No investigation was made of the unknown products accompanying the rearrangement products. There are a number of HCl-elimination products that seem likely candidates, especially since the unknowns were largely absent in the rearrangement of the fluorinated compound **1F**.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for grants in support of this work. R. Wheland thanks the National Science Foundation for a predoctoral fellowship from 1966 to 1970.

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(11) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 92, 1096 (1970).