intermolecular distance for I is given by $r_I = r_1 + r_{2\parallel}$, which is shorter than the distance $r_{II} = r_1 + r_{2\perp}$ for II. Stephen's formula[5] for the pair anisotropy shielding σ_a applied to the two configurations separately becomes

$$(\sigma_a)_I = -2\Delta\chi/3r_I{}^3 \qquad (\sigma_a)_{II} = +\Delta\chi/3r_{II}{}^3 \tag{4}$$

In the *absence of preferred orientation* there will be at any time $Z/3$ solvent molecules in I and $2Z/3$ in II, Z being the coordination number of the first solvent shell which, following Bernstein,[4] can be obtained from $Z = \pi(r_1 + \bar{r}_2)^2/\bar{r}_2{}^2$. The total anisotropy shielding σ_a will therefore be

$$\sigma_a = \frac{-2\pi\Delta\chi(r_1 + \bar{r}_2)^2}{9\bar{r}_2{}^2}\left[\left(\frac{1}{r_I}\right)^3 - \left(\frac{1}{r_{II}}\right)^3\right] \tag{5}$$

Equation 5 can be simplified by replacing algebraic by geometric means (permissible as long as the various radii are not too different). Substituting $r_1 + \bar{r}_2 \approx 2\sqrt{r_1\bar{r}_2}$, $r_1 + r_{2\parallel} \approx 2\sqrt{r_1 r_{2\parallel}}$, and $r_1 + r_{2\perp} \approx 2\sqrt{r_1 r_{2\perp}}$ then results in

$$\sigma_a = -\pi\Delta\chi(r_{2\parallel}{}^{-3/2} - r_{2\perp}{}^{-3/2})/9\bar{r}_2\sqrt{r_1} \tag{6}$$

The main distinction of eq 6 is that it shows σ_a as a pure product of solvent and solute properties. Equations 5 and 6 were tested on gas-to-infinite dilution-in-benzene shifts, measured on methane, neopentane, tetraethylmethane, cyclohexane, and benzene. The results are given in Table I.

Table I. Proton Gas-to-Liquid Shieldings (ppm) of Nonpolar Solutes in Benzene (at 30°)

Solute	$-\sigma_{\text{exptl}}$	$-\sigma_w$	$\sigma_{\text{exptl}} - \sigma_b - \sigma_w$	σ_a Eq 5	σ_a Eq 6	σ_a Eq 7
CH_4	1.051	0.206	0.422	0.966	1.371	0.452
CEt_4	0.893	0.105	0.479			
	(CH_2)			1.049	1.383	0.456
	0.963	0.150	0.454			
	(CH_3)					
CMe_4	0.998	0.212	0.481	1.202	1.456	0.479
C_6H_{12}	0.962	0.186	0.491	1.270	1.488	0.490
C_6H_6	1.001	0.255	0.521	1.366	1.538	0.505

The experimental data were obtained on a Varian A-60A using techniques as described previously.[4] The van der Waals terms σ_w were calculated according to Rummens, *et al.*[4] The bulk susceptibility term σ_b was taken as -1.267 ppm (benzene at 30°), and a value of 9.91×10^{-29} emu was adopted for $\Delta\chi$ of benzene.[6] Table I shows that both eq 5 and 6 predict the correct trend, although the values are too large in both cases. The discrepancies can be taken care of by the introduction of an empirical correction factor (0.408 for eq 5 and 0.329 for eq 6). Recalculation of σ_a then gives a standard deviation $s = \pm 0.033$ ppm ($\pm 7\%$) for eq 5 and $s = \pm 0.017$ ppm ($\pm 3\%$) for eq 6. Although these small variances are probably fortuitous, the results can be termed highly encouraging. Combining the empirical constant of 0.329 with other numerical constants and benzene parameters eq 6 can be rewritten as

$$\sigma_a(\text{ppm}) = +1.08/{}^6\sqrt{V_1} \tag{7}$$

where V_1 is the molar volume of the solute. Values of σ_a according to eq 7 have been given in the last column of Table I. Equation 7 is not only extremely simple and accurate, but shows also the small influence of the size of the solute molecule that has been noted before.[1,3] Of some special interest are the results on tetraethylmethane. Of the observed 0.070 ppm difference in gas-to-liquid shift for the CH_2 and CH_3 groups, 0.045 ppm can be explained in terms of a "site effect" on the van der Waals term.[4] The remaining 0.025 ppm constitutes only 5% of the σ_a shift. This is too low to be realistic and forms in fact the first experimental indication that the site factor for σ_a is unity as predicted before.[3,7]

Extensive further tests of the above model and variations thereof are under way and, together with full details of the present work, will be reported at a later date.

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(5) M. J. Stephen, *Mol. Phys.*, **1**, 223 (1958).

(6) J. Hoareau, N. Lumbroso, and A. Pacault, *C. R. Acad. Sci.*, **242**, 1702 (1956).

(7) F. H. A. Rummens, *Mol. Phys.*, in press.

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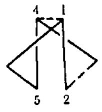
Received January 12, 1970

Stereochemical Course of the Thermally Induced Fragmentation of Bicyclo[2.2.0]hexanes to Diallyls. Pyrolysis of the Dimethyl Bicyclo[2.2.0]hexane-2,3-dicarboxylates

Sir:

When orbital symmetry considerations are applied to the thermal fragmentation of four-membered rings, the $(\sigma^2{}_s + \sigma^2{}_a)$ pathway, *i.e.*, A, is seen to be uniquely allowed.[1] This means that if such a process is concerted, a vicinal *cis* relationship of two groups in the cyclobutane must become *trans* in the olefinic product, and *vice versa.* Recent scrutiny of the pyrolytic cleavage of stereochemically labeled alkylcyclobutanes has disclosed that antarafacial motion by at least one of the developing olefinic moieties is not readily achieved.[2] As a result, little stereoselectivity has been observed. In contrast, the thermolysis of β-lactams[3] and β-lactones[4] proceeds with remarkably high stereospecificity *via* least-motion transition states (retention of configuration), thereby attesting to the ease with which the requisite rotational component can be provided by the carbonyl center.


A



B

We have now examined the stereochemistry of the thermal fragmentation of the three isomeric dimethyl

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(1) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).

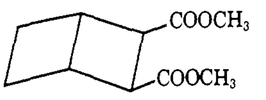
(2) (a) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (b) A. T. Cocks and H. M. Frey, *J. Chem. Soc., A*, 1671 (1969); (c) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(3) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *ibid.*, **92**, 1763 (1970).

(4) (a) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966); (b) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968); (c) M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968).

bicyclo[2.2.0]hexane-2,3-dicarboxylates. This study was prompted by earlier reports[5] that pyrolysis of bicyclo[2.2.0]hexane, the parent system, affords only diallyl. Interestingly, should this fragmentation be concerted, concomitant distortion of both cyclobutane rings as in B is required in the transition state. A further innovation in this instance is the mutual bonding of both newly formed π systems in the product.

exo-cis-Diester **1**, bp 86–87.5° (0.15 mm),[6] was prepared by hydrolysis and esterification (CH_2N_2) of *exo-cis*-bicyclo[2.2.0]hexane-2,3-dicarboxylic anhydride.[7] Catalytic hydrogenation of the known *endo-cis*- and *trans*-dicarbomethoxybicyclo[2.2.0]hexenes[8] afforded **2**, mp 36–39°,[6] and **3**, mp 49.5–51.5°,[6] respectively.



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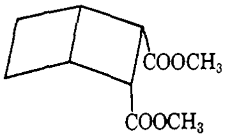

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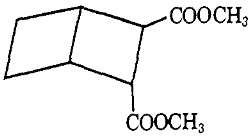


3

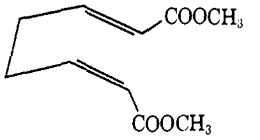
Under conditions where the individual diesters were slowly introduced in the gas phase (8–12 mm, N_2 stream) through a quartz tube packed with quartz chips (contact time ~2 sec), these compounds were seen to be stable to 350°. At 400°, however, the *cis*-diesters **1** and **2** underwent fragmentation to an extent greater than 75%. The *trans* isomer (**3**) was somewhat less reactive and a temperature of 450° was employed in this instance (85–90% conversions). The product compositions were quantitatively analyzed by vapor phase chromatography and the individual components were isolated in pure form by preparative scale vpc for the purpose of unequivocal identification. The results are summarized in Table I.

The reactions of major interest are those leading to the dimethyl 2,6-octadienedioates. Authentic samples of the *cis–trans* (**4**)[6] [$\delta_{TMS}^{CDCl_3}$ 6.77–7.31 (m, 1), 5.72–6.53 (m, 3), 3.73 (s, 6), and 2.17–3.12 (m, 4)] and *trans–trans* isomers (**5**)[6] [$\delta_{TMS}^{CDCl_3}$ 6.77–7.38 (m, 2), 5.76–6.11 (two broad peaks, 2), 3.74 (s, 6), and 2.35–2.50 (m, 4)] were obtained by intermolecular coupling of methyl *trans*-4-bromocrotonate with nickel carbonyl in ether solution.[9] The *cis–cis* isomer **6**[6] [$\delta_{TMS}^{CDCl_3}$ 5.70–6.53 (m, 4), 3.70 (s, 6), and 2.76–2.96 (m, 4)] was prepared by carbonation of the bis Grignard of 1,5-hexadiyne,[10] followed by esterification (CH_2N_2) and controlled hydrogenation ($Pd–BaSO_4$) of the resulting diester. Appropriate control experiments established that no *cis–trans* isomerization of either the starting materials or the products was operative under the reaction conditions. Since both **1** and **2** yield chiefly the *cis–trans* diester **4**, inversion of configuration at one of the cyclobutane centers occurs to the extent of 90%. Of the two single-inversion stereochemical pathways available to **3**, it is seen that the one which leads to the thermodynamically favored *trans–trans* isomer **5** is kinetically preferred. In the total sense, however, 94% inversion of configuration results.

Table I. Product Compositions from the Pyrolysis of the Dimethyl Bicyclo[2.2.0]hexane-2,3-dicarboxylates

	Composition, %[a]			
Diester	**4**	**5**	**6**	**7**
1	80 + 2	9 ± 1		10 ± 0.5[b]
2	79 ± 2	9 ± 3		12 ± 1.5[b]
3	6 ± 0	75 ± 1	18 ± 1	1 ± 0.3[c]

[a] Values represent averages of at least two runs. [b] The *meso* isomer. [c] The *dl* isomer.



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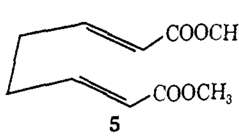

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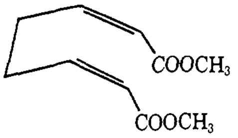

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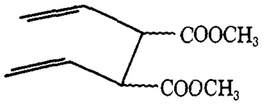

7

Reasonable mechanistic options for these thermal rearrangements are the concerted pathway discussed above and stepwise processes involving initial homolytic rupture of the weak bridgehead bond. In attempting to account for the observation that **1** and **2** afford identical product mixtures, the two mechanistic types differ markedly. In the case of **2**, for example, the concerted bond reorganization would demand not only mutual twisting of both cyclobutane rings as in B, but also that the carbomethoxyl group at C_2 be seriously compressed into the space occupied by the methylene group at position 5. Such a repulsive effect can be expected to result in a substantial destabilization of an already thermodynamically unfavorable transition state and can be ruled out on energetic grounds. Diester **1**, which need not adopt an equally strained transition state, would inevitably rearrange more readily. On this basis, the obtention of an identical product mixture would necessarily be highly coincidental.

In marked contrast, the first stepwise pathway allows for rapid passage of **8** (from **1**) and **9** (from **2**) to a common 1,4-diradical intermediate which can be presumed to possess the thermodynamically favorable chair conformation **10**.[11,12] Subsequent bond cleavage in **10**

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(5) (a) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964); (b) S. Cremer and R. Srinivasan, *Tetrahedron Lett.*, 24 (1960).

(6) Satisfactory elemental analyses (±0.3%) were obtained for all new compounds.

(7) (a) R. N. McDonald and C. E. Reinecke, *J. Org. Chem.*, **32**, 1878 (1967); (b) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

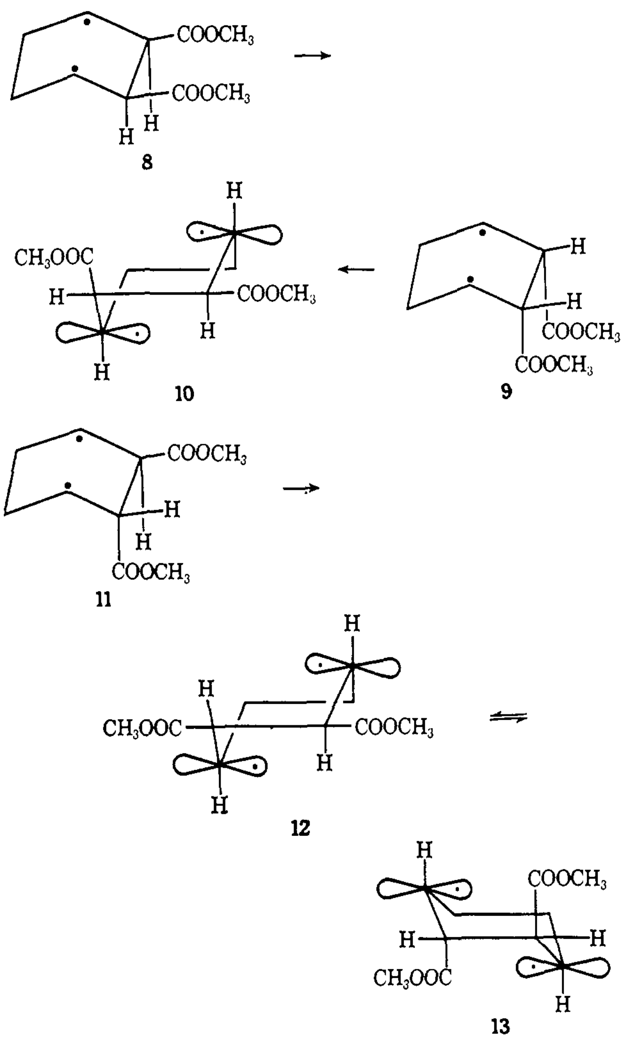
(8) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966).

(9) G. P. Chiusoli and G. Cometti, *Chim. Ind.* (Milan), **45**, 401 (1963). In our hands, the coupling reaction mixture consisted of 68% **4** and 32% **5**.

(10) The general procedure of L. J. Haynes and E. R. H. Jones (*J. Chem. Soc.*, 503 (1946)) was followed. See also L. Lespieau and G. Vavon, *C. R. Acad. Sci.*, **148**, 1332 (1909).

(11) A similar proposal has been advanced by W. R. Roth and M. Martin (*Tetrahedron Lett.*, 3865 (1967)) as a result of their studies of the thermolysis of 5,6-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-enes.

(12) A referee has questioned the basis for our proposal that diradicals **8**, **9**, and **11** prefer to react from chair rather than twist-boat conformations. While we recognize that cyclohexanediones and other cyclohexanes with two trigonal centers in the ring favor the twist-boat conformation in the ground state, two considerations seem to disfavor such an eventuality (at least as the major pathway) in the present instance. The first is purely empirical and concerns the fact that decom-



would reasonably afford chiefly *cis–trans*-diene **4**. Rearrangement of **3** in a comparable stepwise fashion would result in conversion of initially formed **11** to diradicals **12** and **13**.[12]

From the fact that the thermal rearrangements of **1–3** require highly elevated temperatures, explicit recognition of a second stepwise mechanism must be made. Estimates based upon known rates of Cope rearrangement of model compounds suggested that *meso*- and *dl*-**7** should undergo [3,3]-sigmatropic shift at least as fast, if not much faster, than pyrolysis of **1–3**. Therefore, the isomers of **7** become permissible kinetic intermediates. Furthermore, since *meso*-**7** is connected to *cis–trans*-dienedioate **4** by the usual chair-like Cope transition state,[13] whereas *dl*-**7** is similarly linked to the *trans–trans*- (**5**) and *cis–cis*- (**6**) diesters, these substances are also permissible stereochemical intermediates. In actuality, these changes are realized in near-quantitative yield upon resubmission of **7** to the pyrolysis conditions (410°).

Although a specific answer to the question of relative involvement of these two pathways is not available at the present time, the stereochemical results appear to rule out the interpretation[14] that passage of intermediates such as **8**, **9**, and **11** to the corresponding dienes is a synchronous process involving only "electronic reorganization." In the final analysis, it is amusing but pedagogically useful that the high level of antarafaciality attained by one of the double bonds during the pyrolysis of bicyclo[2.2.0]hexane derivatives, although predicted from orbital symmetry considerations, is actually the result of a two-step process.

Acknowledgment. We wish to thank Badische Anilin und Soda Fabrik for their generous gift of cyclooctatetraene which was required in the cyclobutadiene synthesis.

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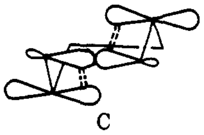
position from twist-boat form D does not account for the stereochemical observations; therefore, if twist-boat forms are involved, bond cleavage is restricted to E. The second consideration arises from the lower relative energy of C (R. Hoffmann, private communication) and the significantly more favorable alignment of the development p orbitals in C relative to D and E.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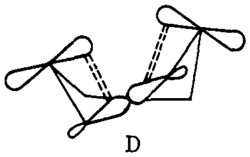
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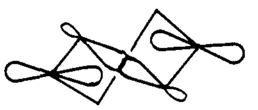
E

[13] W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

[14] For a review of bicyclo[2.2.0]hexane chemistry, see K. B. Wiberg, *Advan. Alicyclic Chem.*, 2, 238 (1968).

[15] National Science Foundation Undergraduate Research Participant, Summer 1969.

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Nucleophilic Substitution at Bivalent Sulfur. Reaction of Alkyllithium with Cyclic Sulfides

Sir:

Epoxides and higher heterocyclics containing oxygen are known to react with alkyllithium by nucleophilic attack at the carbon adjacent to oxygen and subsequent ring opening with formation of the corresponding lithium alkoxides.[1,2] It has been suggested[3] that heterocyclics containing sulfur may behave differently in that carbanions may attack the heterocyclic at the sulfur atom, rather than at an adjacent carbon atom, by analogy to the action of trivalent phosphorus compounds. However, no experimental evidence has been forthcoming to substantiate this view. An unusual attack of nucleophiles on the sulfonium sulfur in the specific case of cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate has recently been demonstrated,[4] but no attempt has been made to generalize this behavior. This communication reports experimental evidence that, under stringent experimental conditions, alkyllithiums attack sulfur-containing heterocyclics *exclusively* at the sulfur atom if severe bond angle distortions are forced upon the atom by the geometry of the molecule.

2-Methylthiacyclopropane, II, was added to an equimolar amount of ethyllithium, I, in tetrahydrofuran

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[1] S. Searles, *J. Amer. Chem. Soc.*, 73, 124 (1951).

[2] E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *ibid.*, 86, 4678 (1964).

[3] N. P. Neureiter and F. G. Bordwell, *ibid.*, 81, 578 (1959).

[4] D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *ibid.*, 91, 3606 (1969).