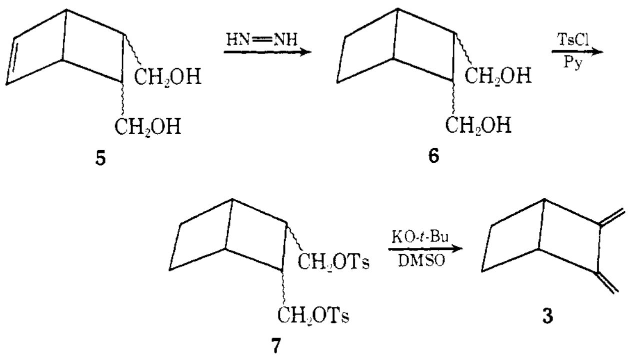
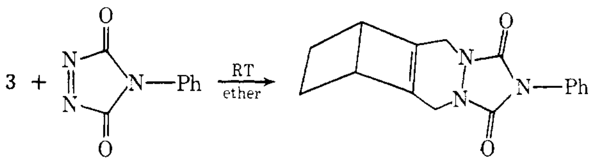
in **3**, the cycloreversion **3** → **4** should be much (at least 28 kcal) more exothermic. Were all of this strain to be released in the transition state for the latter cycloreversion, the activation enthalpy could be less than 18 kcal, a barrier sufficiently small for the expressed purposes. Both experimental and theoretical evidence suggests that the disrotation necessary for maximum strain release is not powerfully[3] (or even at all[8]) opposed by symmetry factors.

The synthesis of **3** was accomplished as shown in Scheme I. The diol **5**[9] was reduced (diimide, acetic acid, room temperature; 94% yield) to the saturated diol **6**: nmr ($CDCl_3$) τ 4.9 (s, 2 H), 6.2–6.6 (m, 4 H), 7.0–8.2 (m, 8 H). Tosylation (tosyl chloride, pyridine, 0–5°, overnight) of the latter gave 66% of the ditosylate **7**: mp 143–145° (MeOH); nmr ($CDCl_3$) τ 2.2 (d, 2 H, J = 8.5 Hz), 2.6 (d, 2 H, J = 8.5 Hz), 5.8–6.0 (m, 4 H), 7.0–8.2 (m, plus s at 7.55, 14 H). Addition of the ditosylate to potassium *tert*-butoxide in DMSO on a vacuum line gave 40–60% of the desired diene (**3**): nmr ($CCl_2{=}CCl_2$) τ 4.8 (s, 2 H), 5.3 (s, 2 H), 6.75 (br s, 2 H), 7.3–8.4 (m, 4 H); uv (MeOH) λ max 238 nm (log ϵ 3.98), 247 (log ϵ 4.05), 257 (sh, log ϵ 3.90); ir (CCl_4) ν 2950 (s), 2875 (s), 1765 (w), 1650 (w), 882 (s), 825 cm^{-1} (s); mass spectrum *m/e* 105, 106, 107 (M − 1, M, M + 1). The uv spectrum of **3** is very similar to that of **1**.[10] Operations involving **3** were performed on a vacuum line, and it was routinely stored at or below −78°.

Scheme I



Reaction with 1-phenyl-1,3,4-triazoline-2,5-dione converts **3** to a bicyclo[2.2.0]-hex-2-ene adduct (**8**) in quantitative yield: mp ($CHCl_3$–Skelly B) 158–160°; nmr ($CDCl_3$) τ 2.3–2.6 (m, 5 H), 5.77 (s, 4 H), 6.5 (br s, 2 H), 7.55–8.4 (m, 4 H); mass spectrum *m/e* 280, 281, 282 (M − 1, M, M + 1).



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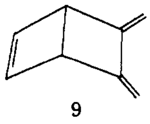

9

The kinetics of the decomposition of **3** in tetrachloroethylene were investigated by means of nmr spectroscopy, measuring the rate of disappearance of the τ 4.8 absorption. Kinetic runs were carried out to greater than 3 half-lives and were treated by least-squares regression analyses of the simple rate equation ln $(A_0 - A_\infty/A_t - A_\infty) = kt$. The decompositions were strictly first order, yielding $k_1 \times 10^4$ sec^{-1} = 1.319 ± 0.002 (51.5 ± 0.5°, 0.5 mM **3**), 2.761 ± 0.029 (60.5 ± 0.5°, 0.5 mM **3**), 2.893 ± 0.027 (60.5 ± 0.5°, 0.25 mM **3**), and 2.107 ± 0.006 (5.65 ± 0.5°, 0.7 mM **3**). The activation parameters calculated from all kinetic runs using a least-squares analysis of the Eyring equation are $\Delta H^{\ddagger} = 17.46 \pm 0.98$ kcal/mol and $\Delta S^{\ddagger} = -22.66 \pm 2.97$ eu. The activation enthalpy for the cycloreversion of **3** → **4** is thus 30 kcal less than that for **1** → **2**. It emerges that there is indeed no very large symmetry-engendered barrier to this reaction and that close to the full amount of the additional strain energy must be released in the transition state. The kinetics indicate that **3** is, in fact, a convenient and facile source for the tetramethylenethane **4** in solution.

It may be worth noting that neither **4** nor *o*-xylylene cyclize appreciably (**4** to bicyclo[4.2.0]octa-1,5-diene; *o*-xylylene to benzocyclobutene) at these temperatures in the liquid phase, though *o*-xylylene does in the vapor phase at elevated temperatures. Apparently these cyclizations have activation requirements that are best satisfied at high temperatures and low concentrations.

It is interesting to note that the much more exothermic cycloreversion of Dewar *o*-xylylene (**9**) to *o*-xylylene also has $\Delta H^{\ddagger} \approx 17$ kcal.[11] Apparently, as predicted by theory, the disrotatory cycloreversion of **9** does have a substantial symmetry imposed barrier, and this approximately nullifies the thermodynamic advantage. The kinetics of the decomposition of bicyclo[2.2.0]hex-2-ene have not been reported, but, as would be expected on the basis of a strongly forbidden disrotatory cleavage mode, it appears substantially more stable than **3**.[12]

Acknowledgments. We thank the Welch Foundation (F-149) for generous support of this work.

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

(10) A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1809 (1955).

(11) C.-S. Chang and N. L. Bauld, unpublished results.

(12) R. N. McDonald and C. E. Reineke, *J. Amer. Chem. Soc.*, **87**, 3020 (1965).

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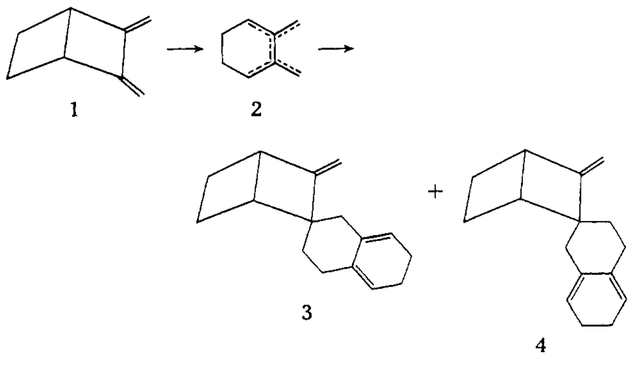
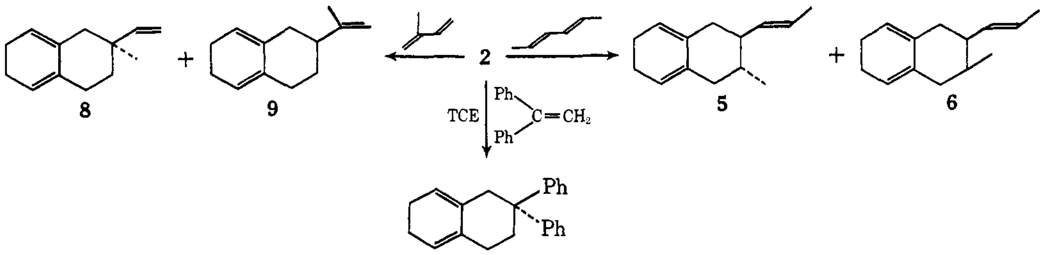
Cycloadditions of 2,3-Dimethylenecyclohexa-1,3-diene, a Tetramethyleneethane Derivative

Sir:

The formation in solution at 40–60° of the novel title compound **2** from a bicyclic precursor **1** has been ac-





8 9 2 5 6 7

complished and demonstrated.[1] The cycloadditions of **2** were seen as of much interest, especially in regard to the structure of **2** and tetramethyleneethanes in general. Several such reactions have been investigated in these laboratories and are described below.

The (first order) decomposition of **1** in tetrachlorethylene (TCE) solution gives hydrocarbon dimers **3** and **4**, corresponding to exo and endo addition, respectively, of **2** to **1**: nmr ($CCl_2{=}CCl_2$) τ 3.30–3.70 (m, 2 H), 4.8 (br s, 2 H), 7.0–9.0 (m, 16 H); mass spectrum *m/e* 212 (M); ir (CCl_4) ν 885 (s, $>{=}CH_2$), 825 cm^{-1} (s, $>{=}C(H)$), *inter alia*. The **3**–**4** mixture was not readily separable, but was further characterized *via* the 1-phenyl-1,3,4-triazoline-2,5-dione adducts. An oily mixture of the four possible adducts was obtained after silica gel chromatography: nmr ($CDCl_3$) τ 2.25–2.70 (m, 5 H), 5.25 (br s, 4 H, olefinic and bridgehead protons α to nitrogen function), 7.2–9.0 (m, 16 H); mass spectrum *m/e* 387 (M); ir ($CDCl_3$) ν 1770 (s), 1715 (vs), 915 (s), 890 (s), and 855 cm^{-1} (s), *inter alia*.

Surprisingly, **2** did not react at all with diethyl fumarate in TCE; the same **3**–**4** mixture as described above was obtained instead. This behavior, incidentally, contrasts sharply with that of *o*-xylylene, which is efficiently trapped under the same conditions.[2] This is true despite the undoubtedly greater exothermicity of cycloadditions involving **2**.[4]

The reaction of **2** with **1** is extremely facile, but heating **1** (40°, 2 days) in 100 vol of neat *trans,trans*-2,4-hexadiene gives, besides 50% of **3**–**4**, 50% of the adducts **5**–**6**, isolated by vpc collection: nmr (CCl_4) τ 4.3–4.9 (m, 4 H), 7.5–8.5 (m and sharp d at 8.3, 13 H), and 9.0 (two d, 3 H, ratio *ca.* 60:40); mass spectrum *m/e* 188 (M). Again the results contrast vividly with those for *o*-xylylene, only a single adduct being isolated by vpc collection in this latter case: nmr ($CDCl_3$, HA-100) τ 3.00 (s, 4 H), 4.57–4.70 (m, 2 H), 7.0–8.2 (m, 6 H), 8.34 (d, 3 H, J = 5.0 Hz), 9.04 (d, 3 H, J = 6.0 Hz).

These results all suggest that **2** reacts by diradical mechanisms and not concertedly with either two- or four-electron systems. Two further observations reinforce this conclusion. The reaction of **2** with 1 equiv of 1,1-diphenylethylene in TCE gives (albeit in only 4% yield) the adduct **7**. Reaction in neat isoprene (40°, 2 days) gives a good yield of adducts **8** and **9** with **8** predominating (65:35) as expected only for a diradical mechanism.[5] The small scale of these reactions and the poor vpc resolution of **8** and **9** precluded their separate characterization,[6] but the nmr spectrum of the mixture, purified by silica gel chromatography, is definitive, especially in comparison with the nmr spectra of the analogous isoprene (and other 1,3-diene) adducts of 1,1-dichloro-2,2-difluoroethylene: nmr (CCl_4) τ 4.0–4.4 (q, J = 10, 18 Hz, $CH_2{=}C(R)H$ of **8**), 4.5 (m, diene C=C(H) of **8** and **9**), 4.8–5.3 (m, $C{=}CH_2$ of **8**–**9**), 7.5–8.1 (m, allylic methylenes of **8**–**9**, methine of **8**), 8.3 (m, $={C(R)CH_3}$ of **9**), 8.4–8.7 (m, nonallylic methylenes of **8**–**9**), 9.11 (s, methyl of **8**; mass spectrum *m/e* 174 (M)). The quoted ratio (65:35) of **8**:**9** is based on the relative areas of the sharp, well-resolved τ 9.1 peak as compared to the total olefinic proton absorptions. The **8**–**9** mixture was further characterized *via* its (four) adducts with **5**. The two adducts of **8** give methyl nmr absorptions at τ ~9 and again the **8**:**9** ratio can be calculated and agrees (67:33) well with that given above.

The preceeding results are those conventionally expected of a triplet state of **2**, but they are not inconsistent with singlet **2** even if one presumes that, *ceteris paribus*, concerted reaction modes are preferred by singlets over stepwise modes. It does appear unlikely that symmetry prohibition alone could explain the inability of **2** to accomplish (highly exothermic) concerted additions to both dienes and dienophiles. Similarly, steric effects (*i.e.*, nonbonded repulsions) seem to be inapposite. There is, though, an appealing stereoelectronic reason for singlet **2** to be unreactive toward concerted cycloaddition. Twisting is evidently favored electronically in tetramethyleneethanes.[7] It is further favored torsionally in **2**. Suprafacial cycloadditions to a twisted structure might be more difficult than normally. Moreover, the rather great reactivity of **2** suggests that activation enthalpies for its reactions may be rather small and hence that entropy may exert greater control over its reactions than is usual in cycloadditions involving molecules less reactive than **2**. Stepwise additions are, of course, favored by entropy over competing concerted ones.

In conclusion, **2** behaves toward cycloaddition as a 2,2′-bisallylic "diradical." The multiplicity of the observed species of **2** is still unknown.

Acknowledgment. We thank the Welch Foundation (F-149) for generous support.

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[1] Preceding communication (C.-S. Chang and N. L. Bauld, *J. Amer. Chem. Soc.*, **94**, 7593 (1972)).

[2] *o*-Xylylene was generated by heating Dewar *o*-xylylene[3] in TCE solution.

[3] F. R. Farr and N. L. Bauld, *J. Amer. Chem. Soc.*, **92**, 6695 (1970).

[4] Though benzenoid resonance stabilization results from the cycloadditions of *o*-xylylene, those of **2** form two new bonds at the expense of only one broken.

[5] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, **86**, 616 (1964).

[6] The isomeric adducts of isoprene with the much more abundant olefin 1,1-dichloro-2,2-difluoroethylene were also ill separated by vpc and were not isolated separately.[5]

[7] B. G. Odell, R. Hoffman, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

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