Macro Rings. XLIII. Rearrangements of and Cycloaddition Reactions across a σ Bond of 1-Vinyl[2.2]paracyclophanes[1]

Mary H. Delton and Donald J. Cram*

Contribution Number 2811 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California 90024.

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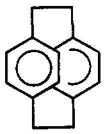
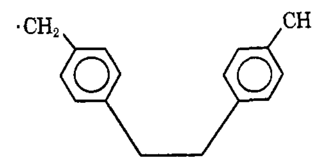
Abstract: Rearrangements and σ-bond cycloaddition reactions of 1-vinyl[2.2]paracyclophane (**1**) and *trans*-β-carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-**2**) have been studied. At 100–165° thermally, or at 25° with irradiation (254 nm), **1** rearranged (ring expanded) to give *cis*-1,2-dehydro[4.2]paracyclophane (**3**) in 90 and 13% yields, respectively. At 100°, *trans*-**2** gave (95%) *cis*-1,2-dehydro-3-carbomethoxy[4.2]paracyclophane (**4**). At 100°, the rates of **1** → **3** and of *trans*-**2** → **4** did not change with change of solvent from benzene to methanol, but the rate of the latter reaction exceeded that of the former by a power of ten. At 100° in dimethyl maleate or fumarate, **1** gave mixtures of **3** (allylic rearrangement), of 2,3-dicarbomethoxy-1-vinyl[4.2]paracyclophane (**5**, product of simple cycloaddition), and of *cis*-1,2-dehydro-4,5-dicarbomethoxy[6.2]paracyclophane (**6**, product of allylic rearrangement and cycloaddition). At 75°, *trans*-**2** in dimethyl maleate also gave products of allylic rearrangement, of simple cycloaddition, and of combined rearrangement and cycloaddition. The difference in yield patterns from **1** in the two esters indicated that the ratio of rates of cycloaddition to simple rearrangement in fumarate ester was about 11 times that in maleate ester. The results are most simply and consistently interpreted in terms of diradical intermediates.

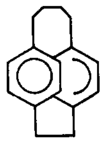
Earlier work demonstrated that the benzyl–benzyl bond of [2.2]paracyclophane and its derivatives cleaved thermally or photolytically to give products of racemization,[2a,b] of hydrogen atom abstraction,[2a–c] of solvolysis,[2b,c] and of cycloaddition.[2a] The results provided strong evidence that at about 200°, [2.2]paracyclophane went to the diradical A. This species collapsed to regenerate starting material, underwent 1,2- to 1,12-cycloaddition reactions to give derivatives of [4.2]paracyclophane, or abstracted hydrogen atoms from suitable donors to give open-chain products.[2a] When photolyzed at various wavelengths in various media, [2.2]paracyclophane gave open-chain products that implied that A could behave like a diradical or a zwitterion, depending on the wavelength of light employed.[2b] Optically active derivatives of [2.2]paracyclophane were found to racemize photochemically with high yields by mechanisms that also involved A. The lability of the σ bond of [2.2]paracyclophane reflects the release of the 31 kcal/mol strain energy of the molecule.[3]



[2.2]paracyclophane

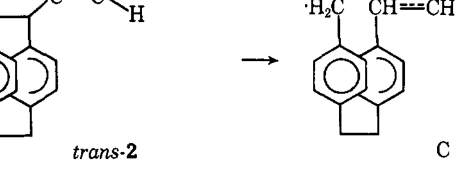


A

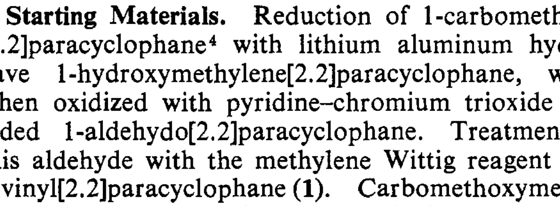


[4.2] paracyclophane

The present paper reports the results of a study of the ring expansions and cycloaddition reactions across the benzyl–benzyl σ bonds of 1-vinyl[2.2]paracyclophane (**1**), and of *trans*-β-carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-**2**). We anticipated that the diradicals B and C derivable from these cycles should be more stable than A, and capable of producing products of simple allylic rearrangement, simple cycloaddition, or of blended rearrangement and cycloaddition.



1 B



trans-**2** C

Results

Starting Materials. Reduction of 1-carbomethoxy-[2.2]paracyclophane[4] with lithium aluminum hydride gave 1-hydroxymethylene[2.2]paracyclophane, which when oxidized with pyridine–chromium trioxide provided 1-aldehydo[2.2]paracyclophane. Treatment of this aldehyde with the methylene Wittig reagent gave 1-vinyl[2.2]paracyclophane (**1**). Carbomethoxymethylene Wittig reagent with the same aldehyde gave *trans*-β-carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-**2**) mixed with a trace of the cis isomer.

Rearrangements. When heated at 165° (neat), vinyl compound **1** gave (90%) 1,2-dehydro[4.2]para-

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[1] The authors warmly thank the National Science Foundation for a grant used in support of this research. M. H. Delton thanks the Regents of the University of California for a First Year Fellowship.

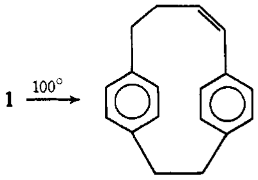
[2] (a) H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 3078 (1967); (b) R. C. Helgeson and D. J. Cram, *ibid.*, **88**, 509 (1966); (c) M. H. Delton and D. J. Cram, *ibid.*, **92**, 7623 (1970).

[3] C. Shieh, O. C. McNally, and R. H. Boyd, *Tetrahedron*, **25**, 3653 (1969).

[4] E. Hedeya and L. M. Kyle, *J. Org. Chem.*, **32**, 197 (1967).

cyclophane (**3**), which was reduced catalytically to [4.2]paracyclophane, identified by comparison with an authentic sample.[5] Photolysis of **1** in methanol with 254-nm radiation[2c] also gave (13%) **3** along with unidentified open-chain materials. When heated at 100° in benzene, *trans*-**2** gave (95%) *cis*-1,2-dehydro-3-carbomethoxy[4.2]paracyclophane (**4**).

First-order rate constant (k_r) estimates were made from two points each for reactions **1** → **3** and *trans*-**2** → **4** at 100° in benzene and in methanol. The reactions were followed by uv analysis ($\pm 9\%$ for **1** → **3** and $\pm 6\%$ for *trans*-**2** → **4**) by Vierordt's method[6] for a two-component system. For **1** → **3**, $k_r \sim 4.5 \times 10^{-5}$ sec^{-1} in benzene (run 1) and $k_r \sim 4.3 \times 10^{-5}$ sec^{-1} in methanol (run 2). For *trans*-**2** → **4**, $k_r \sim 4.7 \times 10^{-4}$ sec^{-1} in benzene (run 3) and $k_r \sim 5.3 \times 10^{-4}$ sec^{-1} in methanol (run 4).



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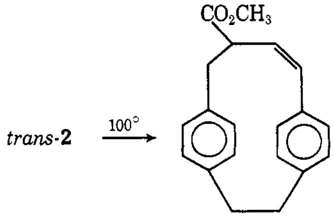
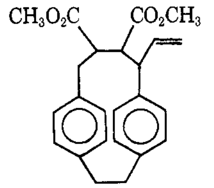


4

Attempts to ring expand 1-carbomethoxy[2.2]paracyclophane and 1-aldehydo[2.2]paracyclophane gave back starting or polymeric materials, although numerous examples are known in which ring expansions do involve ring closure on oxygen.[7]

Competing Rearrangement and Cycloaddition Reactions. When 1-vinyl[2.2]paracyclophane (**1**) was heated at 100° in dimethyl maleate (run 5) or dimethyl fumarate (run 6), both 1,2- to 1,12- and 1,2- to 1,14-cycloaddition reactions occurred in competition with the simple ring-expansion reactions. The products were separated by chromatography into three fractions: a mixture of **1** and **3** (analyzed by uv spectra for the amount of each); a mixture of diastereomers of gross structure **5** (nmr, at least three different methyl groups; *m/e* 378); a mixture of diastereomers of gross structure **6** (nmr, at least seven different methyl groups; *m/e* 378). The tlc and nmr characteristics of the total samples of **5** and of **6** indicated that about the same stereoisomeric mixtures were obtained from maleate and fumarate esters, and that **6** contained both cis and trans isomers. Olefin **3** was shown to be stable to the reaction conditions.

The gross structures of **5** and **6** were demonstrated by their elemental analyses and spectra, particularly nmr and uv. Each of the smaller [*m.n*]paracyclophanes possesses a characteristic uv spectrum.[8] That of **5** was essentially superimposable on that of [4.2]paracyclophane, and that of **6** was very similar to that of [6.3]-paracyclophane (the [6.2] isomer is unknown).



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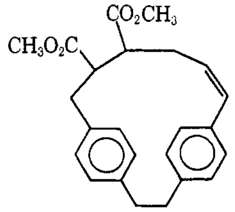
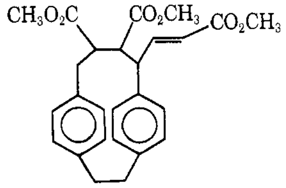


6

When *trans*-**2** was heated at 75° in dimethyl maleate (run 7), and the products similarly separated, trans-**2**, **4**, **7** (diastereomeric mixture), and **8** (diastereomeric mixture) were isolated as separate fractions. These substances were identified by the same methods as those used for the products of runs 5 and 6. Olefin **7** was demonstrated to be stable to the conditions of run 7.



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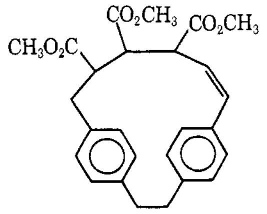

8

The yield patterns from the three competing reactions provided estimates of the three reaction rates in the form of one-point, first-order rate constants, k_r (rearrangement), k_c (cycloaddition without rearrangement), and k_{rc} (rearrangement with cycloaddition). Ultraviolet spectral analyses were used to determine the relative amounts of **1** and **3** in the first chromatographic fractions from runs 5 and 6. Although the cycloaddition reactions must have been bimolecular, k_c and k_{rc} were treated as first-order rate constants since olefinic reactant served as solvent. In estimating the rate constants, k_{obsd} was based on the amount of starting material not recovered, and $k_r = f_r k_{obsd}$, $k_c = f_c k_{obsd}$, and $k_{rc} = f_{rc} k_{obsd}$. In these relationships, f_r = (moles of rearranged product)/(moles of all *products* isolated) etc.; $f_r + f_c + f_{rc} = 1$. In these runs, from 70 to 100% of the starting materials were accounted for. The estimates although crude, are meaningful. For run 5 with **1** in dimethyl maleate at 100°, $k_{obsd} = 5.7 \times 10^{-5}$; $k_r = 3.5 \times 10^{-5}$ sec^{-1}; $k_c = 1.1 \times 10^{-5}$ sec^{-1}; $k_{rc} = 1.1 \times 10^{-5}$. For run 6 with **1** in dimethyl fumarate at 100°, $k_{obsd} = 10.4 \times 10^{-5}$ sec^{-1}; $k_r = 1.2 \times 10^{-5}$ sec^{-1}; $k_c = 3.7 \times 10^{-5}$ sec^{-1}; $k_{rc} = 5.6 \times 10^{-5}$ sec^{-1}. For run 7 with *trans*-**2** in dimethyl maleate at 75°, $k_{obsd} = 6.2 \times 10^{-5}$; $k_r = 2.6 \times 10^{-5}$ sec^{-1}; $k_c = 1.5 \times 10^{-5}$ sec^{-1}; $k_{rc} = 2.2 \times 10^{-5}$ sec^{-1}.

Discussion

Three thermal reactions of 1-vinyl[2.2]paracyclophane (**1**) and of its carbomethoxy analog (*trans*-**2**) have been demonstrated: rearrangement (ring expansion), simple cycloaddition, and rearrangement with cycloaddition. Conceivably, these reactions could

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[5] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).

[6] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, 1958, pp 214–216.

[7] For example, (a) S. J. Rhoads and R. D. Cockroft, *J. Amer. Chem. Soc.*, **91**, 2815 (1969); (b) M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965); (c) D. W. Boykin, Jr., and R. E. Lutz, *J. Amer. Chem. Soc.*, **86**, 5046 (1964).

[8] D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

occur by concerted mechanisms. For example, the thermal rearrangement of **1** → **3** is symmetry allowed provided the migrating benzyl carbon inverts during migration.[9] However, several independent lines of evidence strongly support multistage mechanisms for these reactions, and these are summarized as follows. (1) The three reactions in any one system occur at comparable rates, the largest spread being a factor of 5. Much fortuity would be involved should three unlike (one monomolecular, two bimolecular), concerted reactions go at such comparable rates. (2) The cycloaddition reactions are nonstereospecific, since a similar mixture of both diastereomers and cis–trans isomers were obtained with dimethyl maleate or fumarate as reactants. (3) The parent hydrocarbon, [2.2]paracyclophane, has been shown to undergo homolysis, and the diradical produced adds to dimethyl maleate or fumarate to give the same diastereomeric mixture of cycloaddition products.[2a] This reaction provides a good mechanistic analogy for the mechanisms of reactions of **1** and *trans*-**2**.[10]

The similarity of rates for the three competing reactions in any one system and the nonstereospecificity of the cycloaddition reaction are consistent with a mechanism in which a diradical is produced in these systems as in the parent hydrocarbon, [2.2]paracyclophane. Homolysis is the slow step in these reactions, rearrangement is an intramolecular diradical reaction, and cycloaddition is initially a radical trapping reaction followed (after bond rotations) by a second diradical reaction (ring closure). This general picture of the mechanism of the cycloaddition reaction is particularly attractive since the attempt at initial cycloaddition[2a] was inspired by the fact that styrene forms regular ABAB type copolymers by radical mechanisms with maleate or fumarate esters.[11] The adducts of **1** and these esters constitute formation of an AB copolymer, a reaction that exceeds in rate the formation of either AAAB or ABBB polymer. The consistency of the diradical mechanism with the estimated partial rates for the three reactions is examined in the following paragraphs.

The rate constants for rearrangement of **1** → **3** were essentially identical in benzene ($k_r \sim 4.5 \times 10^{-5}$ sec^{-1}) and in methanol ($k_r \sim 4.3 \times 10^{-5}$ sec^{-1}). The absence of a medium effect on rate indicates the absence of charge separation in the rate-determining stages of the mechanism. The presence of the carbomethoxy group in *trans*-**2** increased the rate by about an order of magnitude, and the reaction was slightly faster in methanol ($k_r \sim 53 \times 10^{-5}$ sec^{-1}) than benzene ($k_r \sim 47 \times 10^{-5}$ sec^{-1}). The tenfold rate enhancement is consistent with the radical-stabilizing ability of the ester group of *trans*-**2** compared to the hydrogen of **1**. The relative reactivity of methyl radicals with methyl acetate *vs.* cyclohexane is 21/4.8.[12]

Equation 1 summarizes the stages envisioned as controlling the yields of products of rearrangement (k_3), cycloaddition without rearrangement (k_5), and cycloaddition with rearrangement (k_6). In this diradical mechanism, k_{-1}, k_3, k_5, and $k_6 \gg k_1$, since homolysis is undoubtedly much slower than covalent bond formation from a diradical. Stages with rate constants k_5 and k_6 probably have a second diradical adduct as a common second intermediate, formed *irreversibly* by addition of the more reactive, nonsubstituted benzyl radical to the olefin. Provided the second diradical only ring closes to give **5** and **6**, for kinetic purposes this more complex scheme reduces to eq 1.

$$\begin{tikzcd} & & \mathbf{3} \\ \mathbf{1} \arrow[r, shift left, "k_1"] & \text{diradical} \arrow[l, shift left, "k_{-1}"] \arrow[ur, "k_3"] \arrow[r, "k_5"] \arrow[dr, "k_6"'] & \mathbf{5} \\ & & \mathbf{6} \end{tikzcd} \tag{1}$$

Application of the steady-state assumption to eq 1 provides eq 2 to 5 which relate the macroscopic and microscopic rate constants. Equation 2 defines k_i, the invisible reaction in which the diradical returns to starting material.

$$k_i = \frac{k_1 \times k_{-1}}{k_{-1} + k_3 + k_5 + k_6} \tag{2}$$

$$k_r = \frac{k_1 \times k_3}{k_{-1} + k_3 + k_5 + k_6} \tag{3}$$

$$k_c = \frac{k_1 \times k_5}{k_{-1} + k_3 + k_5 + k_6} \tag{4}$$

$$k_{rc} = \frac{k_1 \times k_6}{k_{-1} + k_3 + k_5 + k_6} \tag{5}$$

Since k_r did not change in passing from methanol to benzene, it is reasonable to assume that k_1, k_3, and k_{-1} were the same in dimethyl maleate and dimethyl fumarate as they were in benzene and methanol. In benzene and methanol, $k_5 = k_6 = 0$, eq 3 reduces to eq 6, and

$$k_r^{\mathrm{MeOH}} = \frac{k_1 \times k_3}{k_{-1} + k_3} = 4.3 \times 10^{-5}\ \mathrm{sec}^{-1} \tag{6}$$

the value of $k_1k_3/(k_{-1} + k_3)$ for the four media is available. Manipulation of eq 3–6 gives eq 7 and 8, the

$$\frac{k_5 + k_6}{k_{-1} + k_3} = \frac{4.3 \times 10^{-5} - k_r}{k_r} \tag{7}$$

$$k_1 = \frac{(k_c + k_{rc})4.3 \times 10^{-5}}{4.3 \times 10^{-5} - k_r} \tag{8}$$

latter of which allows k_1 to be calculated from k_r, k_c, and k_{rc}.

Equations 7 and 8 rest on the assumption that values of k_1, k_3, and k_{-1} are independent of media. Values of k_1 calculated with eq 8 for runs 5 (dimethyl maleate) and 6 (dimethyl fumarate) are 12×10^{-5} sec^{-1} and 13×10^{-5} sec^{-1}, respectively. The proximity of these values supports the assumption. Values of $(k_5 + k_6)/(k_{-1} + k_3)$ calculated from eq 7 provide estimates of the radical trapping abilities of the medium. In maleate ester (run 5), the ratio was 0.23 whereas in fumarate ester (run 6), the ratio was 2.6. Thus fumarate is about 11 times as efficient in trapping benzyl radicals as is maleate ester. In radical copolymerization studies, the rate constant for capture of radicals by fumarate esters is 6- to 40-fold faster than by maleate

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[9] J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

[10] Unsuccessful attempts were made to prepare 1 and *trans*-2 in an optically active state to see if thermal racemization accompanied the rearrangement and cycloaddition reactions. At 150°, optically active 1-carbomethoxy[2.2]paracyclophane (ref 2c) was found to racemize thermally (M. H. Delton, unpublished results).

[11] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[12] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 495.

esters.[13a] Likewise, methyl radicals react nine times faster with diethyl fumarate as with maleate.[13b]

$$k_i = k_1 - k_r - k_c - k_{rc} \tag{9}$$

Equation 9 provides a means of estimating k_i, the rate constant for the invisible reaction of generation of diradical and its return to starting material. For run 5 with maleate ester, k_i is estimated to be $\sim 6.3 \times 10^{-5}$ sec^{-1}, and run 6 with fumarate ester, the value is $\sim 2.6 \times 10^{-5}$ sec^{-1}. Thus in the poorer radical-trapping medium, about half of the diradicals generated return to starting material. In the better radical-trapping medium, only about a sixth of the diradicals formed regenerate starting material.

Combination of eq 2 and 3 provides eq 10, and combination of eq 4 and 5 gives 11. Values of k_{-1}/k_3 provide an estimate of the relative rates of the allylic diradical going back to 1-vinyl[2.2]paracyclophane *vs.* rearranging to the [4.2]paracyclophane system. For run 5 in

$$\frac{k_{-1}}{k_3} = \frac{k_i}{k_r} \tag{10}$$

$$\frac{k_5}{k_6} = \frac{k_c}{k_{rc}} \tag{11}$$

dimethyl maleate, $k_{-1}/k_3 \sim 1.8$ whereas for run 6 in dimethyl fumarate, $k_{-1}/k_3 \sim 2.2$. The proximity of these values (same within experimental error) adds validity to the assumption that k_1, k_{-1}, and k_3 were solvent independent. It is interesting that closure of the more strained, smaller ring has the favored rate, possibly because of a favored activation entropy. Values of k_5/k_6 give an estimate of the relative rates of ring closure to [4.2]- *vs.* [6.2]paracyclophane systems of the diradical formed by addition of 1 mol of olefin. For run 5 with maleate ester, $k_5/k_6 \sim 1$, whereas in run 6 with fumarate ester, $k_5/k_6 \sim 0.7$. Should the diradical adducts formed from maleate and fumarate persist long enough to lose their stereochemical memories through rotational equilibrations, k_5/k_6 values for the two runs should be identical. Within experimental error, they are the same. The proximity of these values correlates with the spectral and tlc observations that similar balances of diastereomers and of cis–trans isomers were obtained for **5** and for **6** from runs 5 and 6.

Although in principle a similar treatment could be developed for the rearrangement, cycloaddition, and rearrangement with cycloaddition of *trans*-**2**, the data were not available. However, comparison of the values of k_r, k_c, and k_{rc} for run 7 suggests that rate ratios leading to various materials were similar to those observed in the parent 1-vinyl[2.2]paracyclophane system.

Experimental Section

Materials, Instruments, and Techniques. Commercial [2.2]paracyclophane, recrystallized from chloroform, was used. All solvents were reagent grade unless specified otherwise. Fractionally distilled pentane was used. Anhydrous benzene was distilled from calcium hydride; anhydrous methanol was distilled from magnesium turnings. Melting points were taken on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Nuclear magnetic resonance (nmr) measurements were made with a Varian A-60D spectrometer, using 5–20% (w/v) solutions in deuteriochloroform with tetramethylsilane as internal standard. Infrared spectra (ir) were run in spectrograde chloroform or as a Nujol mull on a Beckman IR-5 spectrophotometer. Mass spectra were run at 12 eV on an AEI Model MS-9 instrument. Ultraviolet spectra (uv) were recorded on a Cary Model 14M spectrophotometer in 1-cm quartz cells using absolute ethanol. Weighings of less than 10 mg were done on a Cahn Gram Electrobalance and are accurate to ±0.001 mg. Silica gel for column chromatography was either Baker or Merck chromatographic grade; for thin-layer chromatography (tlc), Brinkmann silica gel G was used on Pyrex plates with appropriate cyclohexane–ethyl acetate mixtures as developer and iodine vapor for visualization. Eluents for column chromatography were uniformly ether–pentane mixtures. All rate tubes were cleaned in the following manner. They were filled with cleaning solution and kept at 100° overnight, washed and rinsed six times with tap water, three times with concentrated ammonium hydroxide solution, and twice with distilled water, and, finally dried in an oven at 120°.

1-Carbomethoxy[2.2]paracyclophane. From 66 g of [2.2]paracyclophane by the literature procedures was obtained 21 g (32% based on consumed starting material) of the ester, which after sublimation gave mp 95.5–96.5°, lit.[4] 96.5–97.5°. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.16; H, 6.78. The nmr spectrum of 1-carbomethoxy[2.2]paracyclophane differed from that of the literature.[4] We observed the following chemical shifts ($CDCl_3$): δ 3.01 (s, 4 H, unsubstituted bridge), 3.45–2.91 (m, 2 H, benzylic H_aH_b), 3.44 (s, 3 H, ester methyl), 4.2–3.87 (m, 1 H, benzylic H_x), 6.32–6.76 (m, 8 H, aromatic).

1-Hydroxymethylene[2.2]paracyclophane. To a slurry of 1.6 g (42.1 mmol) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran, a solution of 7.9 g (29.8 mmol) of 1-carbomethoxy[2.2]paracyclophane in 200 ml of dry tetrahydrofuran was added dropwise at a rate sufficient to maintain reflux. The solution was refluxed overnight, and water and dilute hydrochloric acid were added dropwise to destroy excess reducing agent. The organic material was extracted with ether and the ether extracts were washed with dilute hydrochloric acid, bicarbonate solution, and brine. After drying, the solution was evaporated under reduced pressure to give a white solid, wt 6.5 g, mp 136–137°. Recrystallization of this alcohol from methanol and drying gave an analytical sample of 1-hydroxymethylene[2.2]paracyclophane, mp 137–137.5°, nmr ($CDCl_3$): δ 1.88 (s, 1 H, hydroxyl), 2.1–4.2 (m, 5 H, substituted bridge plus CH_2OH), 3.04 (s, 4 H, unsubstituted bridge), 6.46 (d, 8 H, aromatic). *Anal.* Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.64; H, 7.64.

1-Aldehydo[2.2]paracyclophane. To 15 ml of pyridine (dried over potassium hydroxide) at 0° was added, in small portions, 420 mg (4.20 mmol) of chromium trioxide. The mixture was stirred vigorously and 200 mg (0.84 mmol) of 1-hydroxymethylene[2.2]paracyclophane in 5 ml of pyridine was added all at once. The ice bath was removed immediately and the solution (now brown) was heated to 70° with a heat gun and maintained at that temperature for 2.5 min. The solution was then poured into ice water and extracted with ether. The ether was washed thoroughly with at least five, 50-ml portions of sodium chloride-saturated, 4 *N* sulfuric acid solutions to remove any pyridine. The ether was then washed with 10% potassium hydroxide, water, bicarbonate solution, and brine, and was dried. The ether was removed under vacuum and 184 mg of a white solid was obtained. Acidification of the potassium hydroxide washes afforded 7.6 mg of 1-carboxy[2.2]paracyclophane.

Tlc of the crude product showed small amounts of four other components, all slower moving than the aldehyde. The crude product was chromatographed on 35 g of Baker silica gel and eluted with 250 ml of 2% ether–pentane followed by 250 ml of 5% ether–pentane. The early fractions afforded 180 mg (91%) of 1-aldehydo[2.2]paracyclophane, pure by tlc. Recrystallization of the substance from ether–pentane gave an analytical sample, mp 115.5–116.5° (evacuated). *Anal.* Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.38; H, 6.79.

The nmr spectrum showed a typical abx pattern for the substituted bridge, the x portion being additionally split by the aldehydic proton. The chemical shifts ($CDCl_3$) were: δ 3.03 (s, 4 H, unsubstituted bridge), 2.85–3.70 (m, 2 H, H_aH_b), 4.08 (m, 1 H, H_x), 6.1–6.6 (m, 8 H, aromatic), and 9.98 (d, 1 H, O=CH).

1-Vinyl[2.2]paracyclophane (1). Methyltrimethylphosphonium bromide,[14] 2.27 g stirred under nitrogen in dry tetrahydrofuran,

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(13) (a) F. M. Lewis and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1533 (1948); (b) A. R. Bader, R. P. Buckley, F. Leavitt, and M. Szwarc, *ibid.*, **79**, 5621 (1957).

(14) G. Wittig and U. Schollkopp, *Org. Syn.*, **40**, 66 (1960).

was metallated with 4 ml of 1.6 *M* *n*-butyllithium. At 25° to the stirred solution was added dropwise over 40 min a tetrahydrofuran solution of 1-aldehydo[2.2]paracyclophane (1.5 g, 6.36 mmol). The solution became lighter and a precipitate formed. After refluxing overnight, the mixture was cooled to 25°, and the solid was collected and washed well with tetrahydrofuran. The combined ether layer was washed with water until the water washes were neutral, then dried. Removal of solvent left an off-white solid which contained some starting material by tlc analysis. This solid was chromatographed on 100 g of Baker silica gel and the column was eluted first with 500 ml of pentane, collected in 200-ml fractions. Next, the eluent was 1.5 l. of 5% ether-pentane and 0.5 l. of 10% ether-pentane, collected in 100-ml fractions. Fractions 6 and 7 gave 903 mg of **1** (60%). This was sublimed (56°, 0.02 mm) to give an analytical sample, mp 80–82°. *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.75.

The nmr spectrum of **1** exhibited the following signals: δ ($CDCl_3$) 4.0–2.4 (complex m, 7 H, bridges), 5.0–5.47 (m, 2 H, $=CH_2$), 6.68–6.04 (m, 9 H, aromatic plus $=CH$). The ultraviolet spectrum of **1** very closely resembled that of [2.2]paracyclophane.

Thermal Isomerization of 1-Vinyl[2.2]paracyclophane (1) to *cis*-1,2-Dehydro[4.2]paracyclophane (3). In an evacuated sealed tube was heated 0.137 g of **1** at 165° for 6 hr. After cooling, the tube was opened, and a tlc analysis showed only one component and the absence of starting material. The product was chromatographed on 60 g of silica gel to give, after elution with pentane, 0.123 g (90%) of **3**. Sublimation of this material at 55° and 0.02 mm gave **3**, mp 100–101°. *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.85.

The ir spectrum of **3** gave a band at 695 cm^{-1} assigned to cis HC=CH.[15] No trans HC=CH band at 965 cm^{-1} was present. The nmr spectrum of **3** exhibited aliphatic, vinyl, and aromatic hydrogens. The chemical shifts were: δ 2.3–3.0 (m, 8 H); 5.35–5.94 (complex m, 1 H); 6.2–6.92 (m, 9 H). The ultraviolet absorption spectrum of **3** resembled in general shape that of [4.2]-paracyclophane,[8] but the longer wavelength absorption band of **3** showed a tenfold increase in extinction coefficient and a small shift to longer wavelengths. These facts point to some conjugation of the double bond with the benzene ring. The spectrum exhibited the following characteristics: λ_{max} 222 nm (log ϵ $\sim$ 4.5); λ_{min} 248 nm (log ϵ $\sim$ 3.6); λ_{max} 269 nm (log ϵ $\sim$3.8); $\lambda_{inflection}$ 297 nm (log ϵ $\sim$ 2.9).

Photolysis of 1-Vinyl[2.2]paracyclophane (1) in Methanol at 254 nm under Nitrogen. A solution of 60 mg of **1** in 280 ml of methanol was photolyzed for 1 hr with the U-tube lamp[2c] while nitrogen gas bubbled through the solution continuously. Solvent was removed under reduced pressure and nmr analysis indicated the presence of open-chain material, starting material, and *cis*-1,2-dehydro[4.2]-paracyclophane (**3**). The photolysis product was chromatographed on 15 g of Merck silica gel and the pentane eluate was collected in 30-ml fractions. Pentane eluted 8 mg of **3**, identified by comparison of its nmr spectrum with that of an authentic sample. An unidentified oil was also obtained ($\sim$8 mg).

Reduction of *cis*-1,2-Dehydro[4.2]paracyclophane (3) to [4.2]Paracyclophane. To a solution of 27.3 mg of **3** in 25 ml of 95% ethanol was added 7 mg of 10% palladium on charcoal. The mixture was stirred in a hydrogen atmosphere for 24 hr at 25°. The product (wt 25 mg) was purified by sublimation and by two recrystallizations from ethanol, mp 73.5–74°, undepressed by admixture with an authentic sample of mp 72.5–73°.[5]

***trans*-β-Carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-2).** To a solution of 2 g (8.48 mmol) of 1-aldehydo[2.2]paracyclophane in 125 ml of anhydrous benzene was added 2.75 g (8.61 mmol) of premade ylide, carbomethoxymethylenetriphenylphosphorane.[16] The resulting solution was heated at 50° for 12 hr, after which the benzene was removed under reduced pressure and below 40°. Time and temperature are important due to the facile ring-expansion reaction. The crude product was chromatographed on 350 g of Baker silica gel and eluted with 2 l. of 5% ether-pentane, 2 l. of 10% ether-pentane, and 1 l. of 50% ether-pentane. Two 700-ml fractions were collected followed by 300-ml fractions. Fractions 8–13 contained 1.85 g of *trans*-**2** (74%) which crystallized in needles after removal of most of the ether on the steam bath. Fractions 2 and 3 contained 12 mg of *cis*-**2**.

A portion of *trans*-**2** was recrystallized from chloroform–ether to give needles of mp 151.5–152.5°. *Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.05; H, 6.87.

An analytical sample of *cis*-**2** was prepared by recrystallization of the chromatographed material from methanol, mp 87–89°. *Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.16; H, 6.92. The trans isomer could not be converted to the cis isomer photochemically either *via* direct irradiation or with sensitizer (toluene).

Both cis and trans vinyl esters could be prepared by generation of the ylide *in situ* with *n*-butyllithium as the base, but the yields were generally much poorer; *i.e.*, $\sim$50%.

The corresponding trans ethyl ester was prepared in the same manner from the ethyl ylide. Recrystallization of the substance from ether–pentane gave an analytical sample of mp 134–135°. *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.29; H, 7.18.

The nmr spectra of *trans*- and *cis*-**2** support their configuration assignments. If the α, β, and γ hydrogens are labeled H_a, H_b, and H_c, respectively, the splitting pattern and chemical shifts (60-MHz spectrum) characterize each structure. For *trans*-**2**, H_b (quartet centered at δ 7.45) gave J_{ab} = 15 Hz, J_{bc} = 7 Hz, J_{ac} = 1.5 Hz, with H_a as a doublet of doublets centered at δ 6.05 and H_c as a multiplet centered near δ 3.73. For *cis*-**2**, H_b (quartet centered at δ 6.51) gave J_{ab} = 11 Hz, J_{bc} = 7 Hz, and J_{ac} = 1 Hz with H_a a doublet centered at δ 5.88 and H_c a multiplet centered at δ 5.15. Analogies are as follows: dimethyl fumarate vinyl hydrogens (H_b) occur at δ 6.80 and dimethyl maleate (H_b) at δ 6.48;[17a] in styrene, J_{ab} for the *trans*-vinyl hydrogens is 17.5 Hz and for the *cis*-vinyl hydrogens is 10.9 Hz;[17b] in (*E*)-1-bromo-2-phenyl-1-propene (methyl and vinyl hydrogen trans), J_{ac} = 1.25 Hz, and in the *Z* isomer (methyl and vinyl hydrogen cis), J_{ac} = 1.50.[17c] The fact that H_c gives a chemical shift *ca.* 60 Hz further downfield in *cis*-**2** than in *trans*-**2** correlates with the fact that conformations unique to *cis*-**2** are possible which place the ester group in a deshielding position for H_c. Also interesting is the fact that in the spectrum of *cis*-**2** only, one of the aromatic protons is shifted downfield to δ 6.92 (multiplet) under the influence of the ester group. This shift recalls the ortho and ψ-gem downfield shifts observed for ring-substituted [2.2]paracyclophanes.[18]

Thermal Isomerization of *trans*-β-Carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-2) to *cis*-1,2-Dehydro-3-carbomethoxy[4.2]paracyclophane (4). To a heavy-walled glass tube containing 100 mg of *trans*-**2**, 3 ml of anhydrous benzene was added *via* a syringe. The tube and contents were frozen in Dry Ice–acetone, evacuated to 0.02 mm, flushed with dry nitrogen, warmed, again evacuated, sealed, and heated at 100° ± 0.4 for 3 hr. The tube was then opened and the solvent removed under reduced pressure leaving a white solid. By tlc on silver nitrate impregnated silica gel, it was shown to be pure, uncontaminated by starting material, wt 95 mg. Recrystallization of the substance from ether–pentane gave an analytical sample of mp 96.5–97.5°. *Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.10; H, 6.90.

The ethyl ester derivative of **4** was prepared in a similar manner. It was purified by two distillations in a micro-Hickman flask. Distilled material eventually crystallized, mp 69–71°. *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.29; H, 7.14.

The ultraviolet absorption spectrum of **4** very closely resembled that of **3**, which demonstrated both that **4** contains the [4.2]paracyclophane moiety, and that the double bond is conjugated with the benzene ring, not the ester group. The spectrum of **4** gave these characteristics: λ_{max} 226 nm (log ϵ 4.2); λ_{min} 253 nm (log ϵ 3.5); λ_{max} 270 nm (log ϵ 3.7); $\lambda_{inflection}$ 397 nm (log ϵ 3.1).

***cis*-1,2-Dehydro-3-carboxy[4.2]paracyclophane.** A mixture of 82 mg of **4**, 3 ml of ethanol, 10 ml of water, and 5 ml of a 50% (w/w) potassium hydroxide solution was held at 110° for 15 hr. The acid was isolated by acidification and extraction, wt 55 mg, mp $\sim$200° dec, after recrystallization from ethyl acetate. *Anal.* Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.00; H, 6.55.

First-Order Rate Constant Estimates for the Rearrangement Reactions. Procedure A. Benzene Runs 1 and 3. To a heavy-walled glass tube were added 10 mg of either **1** or *trans*-**2** and 0.5 ml of benzene. The tube and contents were frozen in Dry Ice-acetone,

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(15) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

(16) O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

(17) (a) G. O. Schenck, E. V. Gustorf, and M. J. Jun, *Tetrahedron Lett.*, 1059 (1962); (b) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); (c) D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 2252 (1962).

(18) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).

Table I. Data for Estimation of Rate Constants of Rearrangement (Ring Expansion) of Olefins **1** and *trans*-**2** at 100 ± 0.1°

Run no.	Tube no.	Starting material Nature	Starting material Wt, mg	T_m, min	Solvent	$Am\lambda_1$[a]	$Am\lambda_2$[a]	[b],[b] 10^4 *M*	% b[c]
1	1	**1**	0.639	480	C_6H_6	0.918	0.268	1.85	67.7
1	1	**1**	0.758	480	C_6H_6	1.060	0.316	2.21	68.2
1	2	**1**	0.602	270	C_6H_6	0.889	0.217	1.46	56.8
1	2	**1**	0.680	270	C_6H_6	1.200	0.243	1.55	53.5
2	3	**1**	0.525	270	CH_3OH	0.776	0.173	1.14	51.1
2	3	**1**	0.551	270	CH_3OH	0.773	0.175	1.16	49.2
2	4	**1**	0.579	270	CH_3OH	0.850	0.190	1.25	50.5
2	4	**1**	0.595	270	CH_3OH	0.857	0.194	1.28	50.3
3	5	*trans*-**2**	0.604	30	C_6H_6	0.948	0.220	1.21	58.4
3	5	*trans*-**2**	0.506	30	C_6H_6	0.800	0.180	0.98	55.5
3	6	*trans*-**2**	0.594	30	C_6H_6	0.805	0.199	1.11	54.7
3	6	*trans*-**2**	0.576	30	C_6H_6	0.766	0.208	1.19	60.4
4	7	*trans*-**2**	0.597	30	CH_3OH	0.978	0.228	1.25	61.3
4	7	*trans*-**2**	0.578	30	CH_3OH	0.930	0.220	1.21	61.3
4	8	*trans*-**2**	0.563	30	CH_3OH	0.900	0.215	1.19	61.8
4	8	*trans*-**2**	0.534	30	CH_3OH	0.889	0.208	1.15	62.9

[a] $Am\lambda_1 = \epsilon_a^{\lambda_1}[a] + \epsilon_b^{\lambda_1}[b]$; $Am\lambda_2 = \epsilon_a^{\lambda_2}[a] + \epsilon_b^{\lambda_2}[b]$. For **1** → **3**, $\lambda_1 = 245$ nm, $\lambda_2 = 295$ nm, **1** is a and **3** is b, $\epsilon_a^{\lambda_1} = 3.48 \times 10^3$, $\epsilon_b^{\lambda_1} = 3.64 \times 10^3$, $\epsilon_a^{\lambda_2} = 1.59 \times 10^2$, and $\epsilon_b^{\lambda_2} = 1.37 \times 10^3$. For *trans*-**2** → **4**, $\lambda_1 = 255$ nm, $\lambda_2 = 295$ nm, *trans*-**2** is a and **4** is b, $\epsilon_a^{\lambda_1} = 6.45 \times 10^3$, $\epsilon_b^{\lambda_1} = 3.49 \times 10^3$, $\epsilon_a^{\lambda_2} = 3.37 \times 10^2$, $\epsilon_b^{\lambda_2} = 1.59 \times 10^3$. [b] For **1** → **3**, $[b] = (Am\lambda_2 - 4.57 \times 10^{-2}\, Am\lambda_1)/(1.21 \times 10^3)$ *M*. For *trans*-**2** → **4**, $[b] = (Am\lambda_2 - 5.23 \times 10^{-2}\, Am\lambda_1)/(1.41 \times 10^3)$ *M*. [c] For **1** as starting material, b = **3**, for *trans*-**2** as starting material, *b* = **4**.

evacuated to 0.02 mm, flushed with dry nitrogen, warmed, again evacuated, sealed, and heated at 100° ± 0.5 for approximately one half-life (uv analyses were most accurate for 1:1 mixtures). The solvent of each tube was then evaporated under reduced pressure at <30°. To remove most of the remaining benzene, the compound was redissolved in ether and again rotary evaporated. This was repeated three times and the last traces of benzene were removed by pumping on the sample at 0.02 mm for 2–3 hr.

B. Methanol Runs 2 and 4. The procedure was identical with that used in A except for the following. Liquid nitrogen was used in place of Dry Ice–acetone. Since **1** and *trans*-**2** were insoluble in methanol at 25°, the tubes had to be withdrawn and shaken after being in the rate baths 1.5 min to ensure homogeneity.

C. Ultraviolet Spectral Analyses. The uv analyses were done by Vierordt's method for mixtures of two components[6] on a Cary 14-M spectrophotometer with absolute ethanol, 10.0-ml volumetric flasks, and matched 1-cm quartz cells. The absorption curves for **1**, **3**, *trans*-**2**, and **4** were determined separately, and known mixtures of **1** and **3**, and of *trans*-**2** and **4** were prepared, their curves plotted, and the best two wavelengths selected for analyses of each mixture. At concentrations of about 50% of each component, the agreement between known and calculated concentrations varied from 1 to 4%. To avoid sampling errors, two approximately 0.6-mg samples of each unknown mixture were weighed to ±0.001 mg and analyzed. The rate constants reported in the Results section for runs 1–4 were calculated from the data of Table I. The integrated first-order rate equation, $k = 2.3 \log[100/(100 - \%b)]/t$, was used to calculate *k*'s. Each rate constant is the average of two points, and each %b is the average of two samples taken from each rate tube.

Rearrangements and Cycloaddition Reactions, General Procedure. After preliminary runs had been carried out to establish feasibility, techniques, and times, the following methods were applied to runs 5–7 (preliminary runs gave similar patterns of results). The paracyclophane (**1** or *trans*-**2**) and olefin (dimethyl maleate or fumarate) were weighed into heavy-walled glass tubes, the contents were degassed by two freeze-pump thaw cycles, and the tubes were sealed at about 0.015 mm. After the requisite time in the 100 ± 0.4° or 75 ± 0.4° bath, the tubes were cooled and opened, and the olefinic esters were removed by fractional distillation or sublimation under reduced pressure at temperatures below 40°. The residual products were separated into components by column chromatography (see next section). The recovered olefinic esters (solvents) were less than 2% isomerized (nmr spectral analysis) and contained none of the paracyclophane.

Reactions of 1-Vinyl[2.2]paracyclophane (1) in Dimethyl Maleate (Run 5). From 500 mg of **1** and 5 ml of dimethyl maleate at 100° for 12.5 hr was obtained a product mixture that was chromatographed on 155 g of Baker silica gel. The column was treated with 1 l. of 5% ether–pentane, 1 l. of 7% ether–pentane, and 1 l. of 11% ether–pentane, and the products were collected in 100-ml fractions. Fraction 7 produced 314 mg of a mixture of **1** and **3** qualitatively identified by tlc and nmr spectral comparisons with authentic samples (87% **3** by uv analysis). Fractions 17–23 produced 140 mg of a colorless oil (**5**). Fractions 27–31 gave 146 mg of a solid (**6**) of mp 113–116.5°. A molecular distillation of **5** (1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane) at 200° and 1.6 mm gave an analytical sample, whose mass spectrum gave a molecular ion of *m/e* 378. *Anal.* Calcd for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 76.08; H, 6.92.

The uv spectrum of **5** in 95% ethanol gave λ_{max} 214 nm (ϵ 14,600) and λ_{max} 270 nm (ϵ 384) and was almost superimposable on that of [4.2]paracyclophane.[8] The isomers of **5** gave R_f values of 0.46 to 0.52 on silica gel plates in 20% ethyl acetate–cyclohexane. Three distinctly different methyl ester signals were prominant in the nmr spectrum of **5**, a fact compatible with the expected diastereomers present in the mixture.

The solid, **6**, was sublimed (100°, 0.02 mm) and recrystallized from methanol to give white crystals, mp 114–115.5° (1,2-dehydro-4,5-dicarbomethoxy[6.2]paracyclophane). This material gave a mass spectral molecular ion of *m/e* 378. *Anal.* Calcd for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 76.32; H, 6.71.

The total sample of **6** gave an ultraviolet absorption spectrum in 95% ethanol with λ_{max} 214 nm (ϵ 15,000) and λ_{max} 263 nm (broad with ϵ 2000) and $\lambda_{inflection}$ 295 nm ($\epsilon \sim 320$). The short and medium wavelength λ_{max}'s of **6** occur close to those of [6.3]paracyclophane,[8] and the general shape of the curve resembles those of the other cyclic olefins, **3** and **4**. The nmr spectrum of **6** exhibited seven distinctly different methyl ester signals, a fact that indicates the presence of both diastereomers and cis–trans isomers in the mixture.

Reactions of 1-Vinyl[2.2]paracyclophane (1) in Dimethyl Fumarate (Run 6). A mixture of 150 mg of **1** and 1.5 g of dimethyl fumarate was ground together and heated in a sealed, evacuated tube at 100° for 600 min as a melt. The reaction product was chromatographed on 30 g of Baker silica gel with pentane–ether mixtures as eluting solvent as in run 5. The three fractions were isolated as in run 5. The first fraction (14 mg) exhibited the same tlc behavior as the mixture of **1** and **3** in run 5, and uv analysis showed it to be 82% **3**, and 18% **1**. The second fraction (59.4 mg) isolated as an oil gave the same tlc behavior and the same nmr spectrum as **5** isolated from run 5. The third fraction (90 mg), a solid, gave the same tlc behavior and the same nmr spectrum as **6** isolated from run 5.

Reaction of *trans*-β-Carbomethoxy-1-vinyl[2.2]paracyclophane (*trans*-2) in Dimethyl Maleate. The reaction product from 615 mg of *trans*-**2** and 6 ml of dimethyl maleate at 75 ± 0.4° for 10.5 hr was chromatographed on 150 g of Baker silica gel. The products were collected in 100-ml fractions, with 1 l. of 5% ether–pentane, 1 l. of 10% ether–pentane, 1 l. of 20% ether–pentane, 0.5 l. of 30% ether–pentane, 1 l. of 50% ether–pentane, and 1 l. of 100% ether serving as eluting solvents. Fractions 10 and 11 contained 195 mg of **4**, fractions 13–16 contained 49 mg of *trans*-**2**, fractions 29–31 contained 229 mg of an oil (**8**), and fractions 32–35 contained 161 mg of a solid (**7**).

Recrystallization of **7** (β-carbomethoxy-1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane) from methanol–dichloromethane gave a white solid, mp 150–153°, whose mass spectrum gave a molecular ion at *m/e* 436. *Anal.* Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.54; H, 6.32.

The uv spectrum of **7** very closely resembled that of 1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane (**5**) in shape and the positions of the absorption bands except that in the 250-nm region where **5** has a minimum, **7** showed increased indistinct absorption due to the α,β-unsaturated ester absorption superimposed on that of the ring system. The nmr spectrum of **7** contained five sharp methyl ester singlets, a fact that points to a mixture of diastereomers.

Molecular distillation of **8** (1,2-dehydro-3,4,5-tricarbomethoxy-[6.2]paracyclophane) at 200° and 1.6 mm gave a glass whose mass spectrum exhibited a molecular ion at *m/e* 436. *Anal.* Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.70; H, 6.24.

The uv spectrum of **8** very closely resembled that of 1,2-dehydro-4,5-dicarbomethoxy[6.2]paracyclophane (**6**). The nmr spectrum exhibited six different methyl ester singlets, a fact that points to the presence of both diastereomers and cis–trans isomers in the mixture.

Control Run That Demonstrated Stability of *cis*-2,3-Dehydro[4.2]-paracyclophane (3) to the Conditions of Run 5. When 63 mg of **3** and 0.4 ml of dimethyl maleate were submitted to the reaction conditions of run 5, 62 mg of **3** was reisolated, mp 100–101°, pure by nmr analysis.

Control Run That Demonstrated Stability of β-Carbomethoxy-1-vinyl-2,3-dicarbomethoxy[4.2]paracyclophane (7) to the Conditions of Run 7. Triester **7** (41 mg) and 0.5 ml of dimethyl maleate were subjected to the conditions of run 7. The nmr spectrum of the reisolated **7** (38 mg) was superimposable on that of the starting sample.

Hydrocarbon Thermal Degenerate Rearrangements. V. Stereochemistry of the 1,2-Dimethylenecyclobutane Self-Interconversion and Its Relation to the Allene Dimerization and the Rearrangements of Other C_6H_8 Isomers[1a–c]

Joseph J. Gajewski*[1d] **and Chung Nan Shih**

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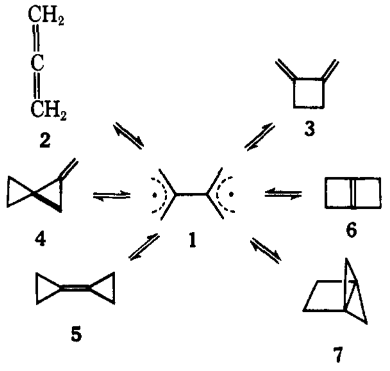
Abstract: The thermally induced degenerate rearrangement of 1,2-bis(dideuteriomethylene)cyclobutane (**8a**) has been studied. Degradative experiments indicate that two products, 4,4-dideuterio-2-dideuteriomethylene-1-methylenecyclobutane (**8c**) and 3,3,4,4-tetradeuterio-1,2-dimethylenecyclobutane (**8b**), are formed in a ratio of $\sim$2:1. This result suggests that the rearrangement proceeds *via* a perpendicular tetramethylenethane diradical (2,2′-bisallyl), **1**. Rotation about the central bond in **1** has been confirmed by observation of the stereospecific thermal rearrangement of *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutane (**14** and **15**). The trans compound **14** gives almost exclusively 3-methyl-2-methylene-*anti*-ethylidenecyclobutane (**17**) and *anti,anti*-1,2-diethylidenecyclobutane (**20**). The cis isomer **15** gives almost exclusively 3-methyl-2-methylene-*syn*-ethylidenecyclobutane (**16**), *syn,anti*-1,2-diethylidenecyclobutane (**19**), and **17**, and the subsequent rearrangement product of **16**, namely, 3-methylene-4-methyl-*trans*-1,4-hexadiene (**21**). These results are consistent with a mechanism in which conrotatory ring opening of the cyclobutane ring occurs to form the orthogonal dimethyl **1**, which then closes to the respective products. The origin of this specificity is discussed as well as the energy surface relating various C_6H_8 isomers and two molecules of allene.

Tetramethyleneethane (TME), or 2,2′-bisallyl diradical (**1**), has been postulated as an intermediate in the thermal dimerization of allenes;[2] it also could be a potential intermediate for the interconversions of allene (**2**), 1,2-dimethylenecyclobutane (**3**), methylenespiropentane (**4**), biscyclopropylidene (**5**), $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**6**), and tricyclo[2.1.1.0^{1,4}]hexane (**7**). Therefore, it has been the subject of numerous, recent investigations.[1,3–6]



The allene dimerization has been shown by Moore to involve either a concerted $_\pi 2_s + {}_\pi 2_a$ cycloaddition or stereospecific formation of the bisallyl diradical followed by stereospecific closure of the diradical.[5] This latter interpretation has some support from Dolbier[7] who found that the rate-determining transition state did not respond to deuterium substitution but the product distribution was influenced by isotopic substi-

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(1) For preliminary communications of these results, see (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) *ibid.*, **91**, 5900 (1969); (c) taken in part from the Ph.D. Thesis of C. N. Shih, Indiana University, March 1971; (d) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

(2) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(3) W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

(4) P. Dowd, *ibid.*, **92**, 1066 (1970).

(5) W. R. Moore, A. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969).

(6) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(7) W. R. Dolbier, Jr., and S.-H. Dai, *J. Amer. Chem. Soc.*, **92**, 1774 (1970).