SYNTHESIS AND THERMAL ISOMERIZATION OF
CIS-3,4-DIPHENYLCYCLOBUTENE

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Abstract—*cis*-3,4-Diphenylcyclobutene has been synthesized, and its thermal isomerization has been studied. Only the conrotatory product (> 99%), *cis, trans*-1,4-diphenylbuta-1,3-diene was observed; the rate constant is described by the Arrhenius equation: $\log k = 13 \cdot 1 - 24 \cdot 5/2 \cdot 303\ RT$.

THE Woodward-Hoffmann rules have proved to be invariably correct in predicting the stereochemical outcome of reactions involving electronic reorganization.[1] An important problem, as yet not thoroughly explored, is an examination of the limitations of the rules and a quantitative measurement of the energy difference between the allowed and non-allowed transition states for these reactions. Several attempts to make estimates of this number for electrocyclic ring opening of cyclobutenes have been made. Using activation parameters for bicyclo[2.1.0]pentene and other homologous bicyclic cyclobutenes, Brauman and Golden[2] have estimated the difference in Arrhenius activation energy for the allowed *vs* non-allowed (probably non-concerted) ring opening to be approximately 15 kcal/mole. Lupton[3] has estimated that this number should be approximately 10–12 kcal/mole, and a direct experimental measure by Doorakian and Freedman[4] places it at > 7·5 kcal/mole.

   Golden and Brauman suggested[2b] that a reasonable *model* for the non-allowed transition state may be a biradical, and they have shown that use of such a model makes it possible to calculate thermochemical properties which are transferrable from one cyclobutene system to another. Recent experiments[5] have demonstrated the quantitative validity of this treatment. If the non-allowed transition state possesses significant radical character, it might be possible to stabilize this transition state by substitution of appropriate groups such as phenyl, and thereby introduce a non-stereospecific component into the ring-opening. The significant lowering of the activation energy by substitution in bicyclic compounds lends support to this approach.[6] A possible candidate, dimethyltetraphenylcyclobutene has been examined by Doorakian and Freedman[4] in an elegant experiment which indicates no apparent leakage into the non-allowed mode; however this molecule is highly crowded sterically and may not provide the optimal experimental test of this idea. The less highly substituted 1,2,3,4-tetraphenylcyclobutenes also appear to react stereospecifically,[7] but these were not examined as exhaustively and may be complicated by the additional phenyl groups on the double bond. Pomerantz and Hartman[8] have studied 3-phenylcyclobutene, but this molecule does not possess sufficient substitution to indicate the stereochemical reaction course.

The hitherto unknown 3,4-diphenylcyclobutenes present an attractive possibility. Previous attempts to isolate them[9, 10] suggest that they possess unusual reactivity and may be quite unstable. We have now prepared cis-3,4-diphenylcyclobutene (1) and report here on its synthesis and on the stereochemistry and activation parameters for the ring opening process.

RESULTS

The preparation of 1 was carried out by the route shown in Fig 1. Solid phase irradiation of the metastable β-crystalline form of trans-cinnamic acid yielded β-truxinic acid exclusively.[11] Although electrolysis of β-truxinic acid carried out under Kolbe conditions by Paudler was reported not to yield the desired cyclobutene,[9] when we carried out the electrolysis[12] on platinum electrodes in 10% aqueous pyridine containing 2 equivalents of triethylamine at 0°, a 24% yield of 1 was obtained with apparently no other hydrocarbon products.
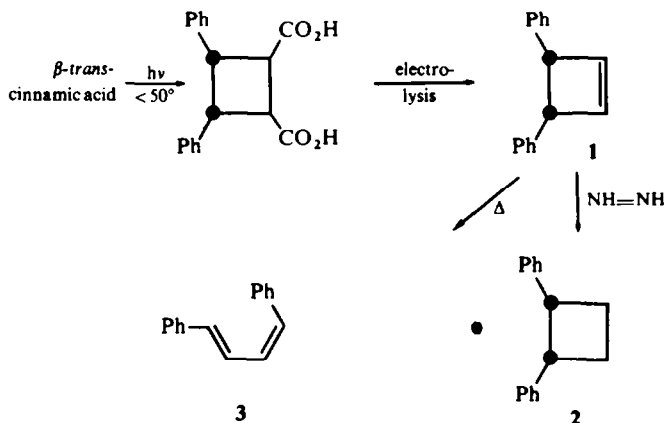

FIG 1. Synthesis and structure proof of cis-3,4-diphenylcyclobutene.

The structure and stereochemistry of 1 follows from the method of synthesis; the reduction of 1 with diimide to the known[13] cis-1,2-diphenylcyclobutane (2); and the conversion of 1 by heating to cis,trans-1,4-diphenylbuta-1,3-diene (3).[14]

Analysis by vpc of the product distribution obtained upon pyrolysis of a sample of 1 in CCl4 at 100° showed the ring opening to give the allowed product 3 with stereo-specificity of >99%.

The kinetics of the isomerization 1 to 3 were followed spectrophotometrically in hexadecane solvent at temperatures ranging from 26·8 to 75·1°. The calculated first-order rate constants are presented in Table 1. The results are accommodated by a least squares fit to the Arrhenius equation:

$$\log k = 13\cdot1 - 24\cdot5/2\cdot303\, RT$$

The Arrhenius plot of these data is shown in Fig 2. The standard error in E_a is about

TABLE 1. ISOMERIZATION RATE CONSTANTS

$T(°K)$	k (sec^{-1})	% reaction[a]
300·0	1·80 × 10^{-5}	75
300·0	1·82 × 10^{-5}	51
309·9	6·68 × 10^{-5}	51
319·1	2·12 × 10^{-4}	75
319·1	2·13 × 10^{-4}	54
327·6	5·84 × 10^{-4}	75
327·6	5·72 × 10^{-4}	56
332·4	9·77 × 10^{-4}	50
332·5	1·01 × 10^{-3}	52
337·4	1·76 × 10^{-3}	75
337·5	1·67 × 10^{-3}	61
337·5	1·78 × 10^{-3}	74
342·6	2·97 × 10^{-3}	75
348·3	5·43 × 10^{-3}	76

[a] extent of reaction used to fit rate constants

0·1 kcal/mole; this merely represents the statistical reproducibility of the data. Small systematic errors may well be present and would affect the value of E_a but not the fit.

DISCUSSION

Within the limit of experimental error, only ($>99\%$) the allowed product, cis,trans-1,4-diphenylbutadiene, is formed in the thermal isomerization of cis-3,4-diphenylcyclobutene. The rate of the isomerization is substantially enhanced over that of cyclobutene;[15] in fact, diphenylcyclobutene is not stable at room temperature. The activation energy for isomerization is 24·5 kcal/mole. Since we may have expected biradical transition state to be substantially stabilized, the appearance of only the allowed product must be explained. This could result from some combination of two factors: an extraordinarily large energy difference between allowed and non-allowed transition states, and stabilization of the allowed transition state by phenyl substitution.

We can estimate the stabilization expected from substitution in a biradical transition state. If the unsubstituted non-allowed transition state has ca 10 kcal/mole resonance energy (allyl resonance),[2b] substitution would add 12·5 kcal/mole for the first phenyl, and less for the second (the cinnamyl resonance energy is unknown, but it is probably close to that for benzyl).[16] Thus we conclude that the non-allowed substituted transition state lies only slightly above the allowed unsubstituted one.

Previous work by Freedman,[4, 7] Battiste,[17] Pomerantz[8] and Marvell[18] et al. indicated that allowed transition states are stabilized by phenyl substitution. From the work of Frey[19] and Srinivasan,[20] it is to be expected that similarly substituted cyclobutenes will have similar A factors. Analyzing our data and those of Freedman and Pomerantz by assuming a constant A factor, changes the precise values of the E_a's, but it does not affect the conclusion. Each additional phenyl group stabilized the allowed transition state electronically by about 5 kcal/mole. The steric effects observed

in other 3,4-disubstituted cyclobutenes[19, 20] suggest that the *cis*-compounds will be retarded slightly in rate while the *trans*-compounds will be accelerated. Thus, the stabilization observed for the reaction of *cis*-3,4-diphenylcyclobutene (8 kcal/mole over cyclobutene) is probably a minimal value.

The origin of the stabilization by phenyl in a concerted reaction is of substantial interest. It is expected that the stabilizing effect of phenyl groups on the allowed transition state is probably not as great as the effect on the non-allowed one. This results from considerations of perturbation theory, which suggests that stabilization will be greatest for the least stable system; particularly if it is essentially biradical in character. Nevertheless, the stabilization observed in the allowed case, *ca* 5 kcal/mole for each phenyl, is so large (almost half of the benzyl resonance energy[16]) that it suggests that the interaction is an unusual one.

Examination of molecular models suggests that during the course of the electro-cyclic cyclobutene isomerization, appreciable electron density may occur in areas in which there is no bonding. That is, the "tails" of the hybrid orbitals at the termini of the π-system do not overlap effectively with other orbitals in the cyclobutene-butadiene system. Thus, it might be expected that some electron density could be delocalized onto an appropriate substituent if the overlap and geometry were satisfactory.

As expected, HMO calculations correctly indicate that the thermal conrotatory transition state is substantially better than that for either a disrotatory or a "birdaical" (non-interacting) one. Addition of one or two phenyl rings at the 3 and 4 positions has essentially the same effect on each of the processes—conrotatory, disrotatory and
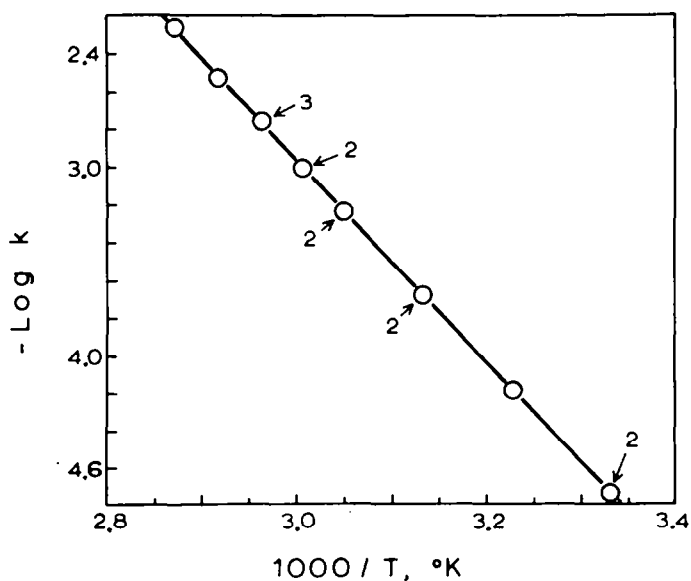

Fig 2. Arrhenius plot for isomerization of *cis*-3,4-diphenylcyclobutene. Numbers indicate overlapping points.

biradical. There is a small additional stabilization in the disrotatory and biradical transition states, but it is relatively minor. These results are essentially independent of the parameters chosen to describe the system. Thus, the HMO calculations are consistent with the observations.

In summary, we have now prepared and studied the isomerization of the relatively unstable *cis*-3,4-diphenylcyclobutene. We have found that phenyl groups can stabilize the transition state for concerted electrocyclic reactions and suggest that such stabilization may be the result of the inability of the orbitals being transformed to overlap with each other with complete effectiveness. While the non-allowed transition state is probably also stabilized, it is not lowered sufficiently in energy to drop below that for the concerted reaction.

EXPERIMENTAL

Microanalyses were carried out by E. Meier and J. Consul, Stanford University Microanalytical Laboratory. NMR spectra: Varian T-60; IR spectra: Perkin-Elmer 421; UV spectra: Cary 14. M.ps are uncorrected.

β-*Truxinic acid* was prepared by irradiation of β-*trans*-cinnamic acid using the method of Cohen, *et al.*[11] with modifications; the following procedure was found to be most convenient. Ether (1 l.) cooled to 5° was saturated with *trans*-cinnamic acid (Matheson, Coleman and Bell) and filtered through a cotton plug. Then cold (5°) light petroleum (2 l.) (30–60°) was added quickly with swirling, and the ppt of β-*trans*-cinnamic was collected by filtration and stored in an ice-box until use. The acid was irradiated with a 400-W, med press Hg arc lamp in 4 g batches in a rotating 2 l. pyrex flask cooled by partial immersion in a running water bath. In this way the temp was kept well below 50° (conversion to the more stable α-crystalline form begins at this temp). Irradiations were carried out for 12–24 hr, and work-up was accomplished by extraction with 50 ml of ether to remove any unreacted cinnamic acid, followed by filtration of the insoluble β-truxinic acid. Material prepared in this manner had m.p. 200–208° (lit.[21] 209°). Conversions of 50% or more could be realized routinely. The truxinic acid was used without further purification.

cis-3,4-*Diphenylcyclobutene* (**1**) was prepared by electrolysis of β-truxinic acid in 10% aq pyridine containing 2 equiv of triethylamine using Pt electrodes at 250–300 v and currents ranging from 0·05 to 0·20 amps.[12] The soln was stirred rapidly and the temp maintained at 0 to − 10° by cooling with a − 80° bath. Work-up in the cold (5°) consisted of adding an amount of water equal to the volume of pyridine soln, extracting twice with pentane (total volume of pentane also equal to pyridine volume). The pentane was washed with several portions of dilute acid, dilute base, and finally water. Removal of the pentane *in vacuo* at 0° gave a crude oil which NMR showed to be quite pure. For example, 500 mg (0·0017 moles) β-truxinic acid in 25 ml of 10% aq pyridine containing 1·0 ml triethylamine, was electrolyzed for 6 hr and yielded after work-up 146 mg of crude product (24%). The material could be further purified by preparative TLC or by passage down a short (1″) alumina column in pentane. Crystallization could be effected from MeOH at − 35°, m.p. 37–38·5°. (Found: C, 93·3; H, 6·8. Calc for $C_{16}H_{14}$: C, 93·2; H, 6·8%); NMR: broad singlet at 3·05 τ (10H); singlet at 3·5 τ (2H); singlet at 5·5 τ (2H); IR: major bands at 691, 1448, 1491, 1598, 2904, 3032 cm⁻¹.

Structure proof. Reduction of **1** (150 mg) in MeOH with a 100-fold excess of diimide (generated from potassium azodicarboxylate with AcOH) yielded after purification on VPC (QF-1) 80 mg of a product identified as *cis*-1,2-diphenylcyclobutane on the basis of its m.p. of 38–39° (lit.[13] (38–39°) and its NMR spectral properties which were wholly consistent with those published[13] for this compound and which clearly distinguished it from the *trans* isomer. In addition, when a sample of **1** was heated in cyclohexane at 85° for 1·5 hr (ample time to effect complete isomerization) and the UV spectrum of this soln recorded, it was found to be essentially superimposable with that published for *cis,trans*-1,4-diphenylbutadiene, and clearly distinguishable from the other geometrical isomers of 1,4-diphenylbutadiene.[14] The VPC retention characteristics were also identical with those of an authentic sample of the *cis,trans* isomer.

Product distribution study by VPC. A sample of **1** pyrolized in CCl₄ at 100° for greater than 10 half-lives was analyzed for products on a 10′ × ¼″ column (5% Fluorosilicone QF-1 on 80/100 mesh Chrom. G, AW and DMCS) at a flow rate of 43 ml/min. Although some (ca 1%) of the *trans,trans* diene was observed under these conditions, it was shown to arise from isomerization of the *cis,trans* compound in the injector block;

thus the ring opening reaction was observed to give greater than 99% of the *cis,trans* diene as product.

Kinetics. The kinetics of the transformation of 1 to *cis,trans*-1,4-diphenylbutadiene were measured in hexadecane soln by monitoring the increase in absorption at 314 nm, a wavelength corresponding to an absorption maximum in the product. A Cary Model 14 spectrophotometer fitted with a thermostatted cell compartment was employed for this purpose. The reaction was carried out directly in a normal 1 cm square quartz cell (rinsed with base before each run); the temperature during a run was monitored by a glass-encased thermocouple immersed in the cell. The observed kinetics were strictly first-order and the rate constants were obtained from a programmed least squares analysis of the first-order rate equation.

$$-\ln(OD - OD_t) = kt + \text{const} \, (OD = \text{optical density})$$

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