THE SYNTHESIS AND VALENCE ISOMERIZATION

OF 1,2-DIPHENYLCYCLOBUTENE

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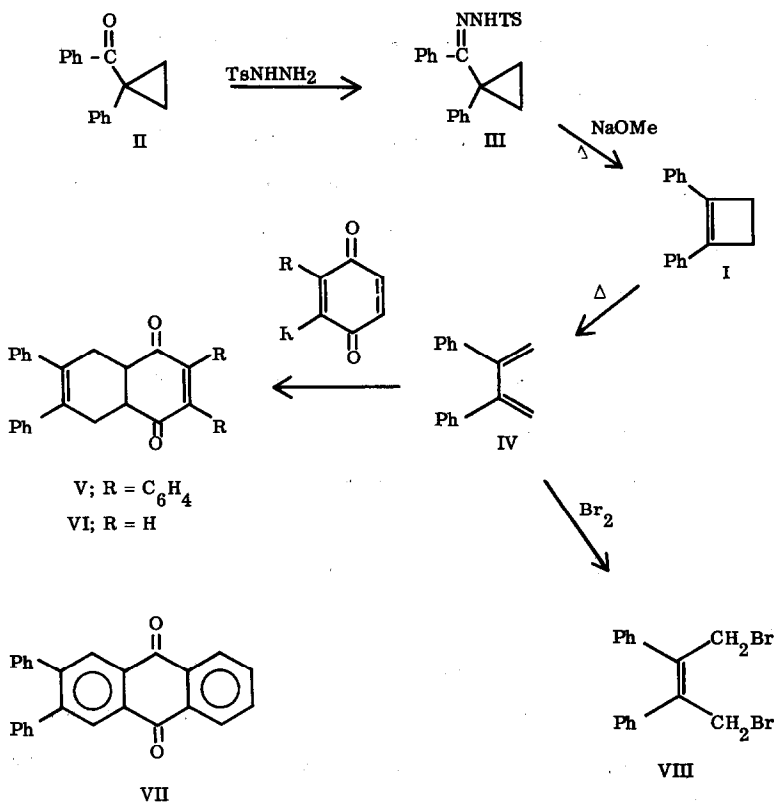
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In connection with a study of the spectral properties and dienophilic

reactivities of a series of diphenylcycloalkenes we required a convenient

source of 1,2-diphenylcyclobutene(I), an unknown hydrocarbon at the beginning

of this study. The synthetic scheme chosen for this hydrocarbon involved an

aprotic Bamford-Stevens reaction[1] of the tosylhydrazone of known 1-phenyl-

cyclopropyl phenyl ketone(II)[2]. Two recent syntheses of I by alternative

routes [3,4] prompt us to report at this time the results of our preparative

work, together with some initial findings of a kinetic study of the valence

isomerization of I to 2,3-diphenylbutadiene. Although the stereospecificity

of valence isomerizations of 3,4-disubstituted and 1,2,3,4-tetrasubstituted

cyclobutenes has received intensive study in the last several years, [5] there

have been comparatively few quantitative studies of the effect of substituents

on the cyclobutene-butadiene isomerization rate. A kinetic study of the

valence isomerization of 1,2-diphenylcyclobutene is of particular interest in

light of recently reported rate data for the isomerization of cis- and trans-1,2,3,4-

tetraphenylcyclobutene[6]

Treatment of 1-phenylcyclopropyl phenyl ketone(II) with tosylhydrazine

in ethanol containing trace amounts of acetic acid gave a 71% yield of the

tosylhydrazone III, m.p. 191-193° (dec.), after 7 days reflux. Anal. Calcd.

for $C_{23}H_{22}O_2N_2S$: C, 70.75; H, 5.68. Found: C, 70.91; H, 5.80. The base-

catalyzed decomposition of III was then carried out in N-methyl-2-pyrrolidone

at 120°, using freshly prepared sodium methoxide as base. Nitrogen evolution

at this temperature was immediate and essentially complete after 12 min.

Alumina chromatography of the crude reaction product led to a colorless oil

which crystallized from methanol at -78° to give a 76% yield of 1,2-diphenyl-

cyclobutene as colorless plates, m.p. 51-53.5°. An analytical sample obtained

after two additional recrystallizations had m.p. 53-54°. Anal. Calcd. for

$C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.04; H, 6.97.

The ultraviolet spectrum of I($\lambda_{max}^{isooctane}$ 227.5(ϵ 24,100), 236(sh.)(13,500),

297(18,400), 307(sh.)(17,500) and 322 mμ(inf.)(10,800)), which is in complete

accord with that reported by Dodson and Zielske,[3] is striking in that it more

closely resembles the spectrum of trans-stilbene than that of cis-stilbene,

specifically with regard to the position of the long wavelength maximum and

the vibrational structure of the two major absorption bands. Some features of

the cis-stilbene chromophore are retained in the spectrum, the greater intensity

of the shorter wavelength band being most notable. We interpret the above

spectral data to mean that the phenyl rings of I are nearly coplanar with the

cyclobutene ring, although the length of the chromophore along the long axis

is still less than that for <u>trans</u>-stilbene[7]. Support for this conclusion

is provided by the n.m.r. spectrum of I in $CDCl_3$, which shows a complex

multiplet centered at 2.58 𝜏 together with a sharp singlet at 7.24 𝜏 in the

area ratio of 2.4:1.0 respectively. The aromatic protons of <u>trans</u>-stilbene

appear as a complex multiplet centered at about 2.6 𝜏, whereas <u>cis</u>-stilbene

shows only a sharp singlet at 2.82 𝜏[8].

The valence isomerization of I to 2,3-diphenylbutadiene(IV) at elevated

temperatures was demonstrated by spectroscopic as well as chemical means. A

neat sample of I was heated in an open tube at 190° for 3 min. (ca. 1.3 half-lives)

and the n.m.r. spectrum of this material immediately examined. The appearance

of an AB quartet centered at 4.77 τ (J = 1.8 cps) signaled the formation of butadiene

IV. From the relative areas of the cyclobutene methylene proton peak and the

butadiene methylene proton peaks the extent of isomerization was estimated to be 54%,

which is in line with the calculated half-life at this temperature (see Table I).

Addition of bromine to a chloroform solution of a sample of I that had been heated

at 190° for 7 min. (ca. 3 half-lives) led to the isolation of dibromide VIII, m.p. 148-

150.5° (lit.[9] m.p. 145-147°). Refluxing a xylene solution of I for 26 hrs. in the

presence of an equivalent of 1,4-naphthoquinone or p-benzoquinone produced the

tetrahydroquinone derivatives V, m.p. 165-166° (lit.[9] m.p. 175-176°), and VI,

m.p. 161-163° (lit.[9] m.p. 163°), in yields of 52% and 25% respectively. Further

characterization of V was accomplished by oxidation to 2,3-diphenylanthraquinone(VII),

m.p. 211-212° (lit.[9] m.p. 211-212°). The isolation of crystalline IV was prevented

by the formation of considerable quantities of polymeric material in pyrolyses run

for longer than 2 half-lives. Thus n.m.r. examination of a sample of I that had

been previously heated at 155° for 3.5 hrs. (ca. 5 half-lives) revealed only the

presence of polymer and a trace of unchanged I.

Rate measurements in dilute decalin solution (10^{-3} $\underline{M}$) showed good first order

behavior, the I to IV isomerization being followed in the ultraviolet by rate of

disappearance of the long wave length absorption band of I now shifted to 299.5 mμ in

this solvent. The rate constants obtained at two temperatures are given in Table I and

lead to rate expression: $k = A \exp(-E_a/RT) = 10^{12.8} \exp(-32,000/RT) \sec^{-1}$. The fre-

quency factor, log A=12.8, is comparatively normal, reflecting a fairly small entropy of

activation, which is in line with the unimolecular character of the reaction[10a].
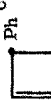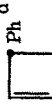
Although reaction rates in solution are not strictly comparable to those in the gas phase, unimolecular reactions of the type involved here normally give closely agreeing results in the two phases[10b]. At any rate, a large solvent effect for the cyclobutene to butadiene isomerization would not be expected, and from the data in Table I one obviously concludes that phenyl substituents at the vinyl positions of cyclobutene have little or no effect on the rate of valence isomerization. This result is considered striking in view of Frey's report[11] that 1, 2-dimethylcyclobutene isomerizes at about one-tenth the rate of cyclobutene[12]. Frey attributed this significant rate lowering to a lengthening of the ring double bond by the stabilizing methyl substituents, thus decreasing ring strain and the rate of ring opening. If this were the only factor operating, then an even larger rate lowering effect would be predicted for the phenyl substituents in I, contrary to the observed results. At the moment it seems quite possible that the observed rate of isomerization of I results from a fortuitous balancing of steric and electronic factors which cannot be properly assessed at this time. On the other hand the lower isomerization rate for 1,2-dimethylcyclobutene as compared to cyclobutene may be largely attributed to steric factors resulting from increased methyl-hydrogen and methyl-methyl interactions in the transition state.

Examination of the relative rates of isomerization in Table I clearly establishes that the rate accelerations observed for cis- and trans-1,2,3,4-tetraphenylcyclobutene arise almost entirely as a consequence of the allylic phenyl substituents. Since even for the trans -tetraphenyl isomer one would expect significant steric interactions to be present in the transition state for conrotatory ring opening,[13] the rate accelerations in Table I probably

represent only a lower limit for those anticipated for cis - and trans-3,4-diphenylcyclobutene.

Further study of the effect of substituents on the rate of cyclobutene valence isomerization is in progress. Support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR 738-65, and in part by the National Science Foundation, Grant No. GP-3352, is gratefully acknowledged. The authors are also indebted to Professors W. M. Jones and J. A. Deyrup of this department for helpful discussions.

TABLE I

Substituent Effects on the Kinetics of Cyclobutene Valence Isomerization

Cpd.	T(°C)	$10^4 k$ (sec.$^{-1}$)	E_a (kcal./mole)	log A	$10^4 k_{150°}$ [e] (sec.$^{-1}$)	Rel. k 150°	Ref.
(cyclobutene) [a]	150	1.9-2.0	32.5 ± 0.5	13.1	1.9-2.0	1	12
Me Me [a]	149.7	0.162	36.0	13.8	0.17	0.09	11
Ph [b]	138.4 ± 0.2 / 155.1 ± 0.2	0.548 ± .012 / 2.79 ± .09	32	12.8	1.9	1	this work
Ph Ph [c]	50	0.8	25	12.8[f]	7500	4000	6
Ph Ph [d]	24	0.5	21	11.1[f]	18,000	9500	6

[a] Kinetic data obtained in the vapor state.   [b] 10^{-3} M solutions in decalin.   [c] Solvent unspecified.

[d] Solvent THF.   [e] Calculated from data at other temperatures where necessary

[f] Calculated from data in Ref. 6.

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14. The fairly small frequency factor found for isomerization of trans-
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     of the developing π-centers in the transition state. A similar situation
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