of **5** was produced in a various amounts in all cases, subtractions were made for the yields of the diene adducts given hereafter.
(10) The assignment is based on the NMR analysis. The vicinal coupling constants ($J_{2,3}$) were in good agreement with those for exo-exo and exo-endo protons in the bicyclo[2.2.1]heptyl system (see Experimental Section). Moreover, four methylene protons at the acetal ring appear as a singlet in **6b** and **6c**, whereas those in **6a** appear as a nearly A_2B_2 pattern. Only the exo cyclopropyl group seems to exert its anisotropy on the acetal ring protons.
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Trends in Disproportionation Equilibria and Kinetics of Radical Anions Derived from 1,2-Diphenylcyclobutene, -cyclopentene, and -cyclohexene

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Abstract: Sodium salts of radical anions and dianions of 1,2-diphenylcyclobutene, -cyclopentene, and -cyclohexene were characterized through their spectra. The equilibrium and kinetics of disproportionation (eq 1) were studied. The results showed that K_{dispr} increases from 0.15 for the butene system to 110 for the pentene and to 3000 for the hexene. Rate constants k_1's are only slightly affected by the size of the ring, being 2.4×10^7, 3.8×10^7, and $\sim 9 \times 10^7$ M^{-1} s^{-1} for the four-, five-, and six-membered rings, respectively, whereas the rate constants of the reverse reactions, k_{-1}, strongly decrease along this series from 1.6×10^8 to 3.5×10^5 and again to 3×10^4 M^{-1} s^{-1}. Disproportionation of sodium salts of *trans*- and *cis*-stilbenides was thoroughly discussed. It was shown that $K_{\text{dispr},T^{-}\cdot,Na^{+}}$ (0.03) is 10 000 times smaller than that of the cis isomer (250) implying that the strain operating in *cis*-stilbene and its radical anion is alleviated in the dianion. Literature pertaining to the shape and thermodynamics of the pertinent species was fully reviewed. ^{1}H and ^{13}C NMR spectra and mass spectra of the investigated diphenylcycloalkenes were studied and discussed.

Studies of disproportionation of aromatic radical anions reported previously[1-4] have now been extended to radical anions derived from 1,2-diphenylcyclobutene (B), 1,2-diphenylcyclopentene (P), and 1,2-diphenylcyclohexene (H) with the intention of investigating how the strain of the ring affects the equilibria and rates of their disproportionation. We restricted this investigation to systems involving sodium salts of the respective radical anions dissolved in tetrahydrofuran. Under our conditions all the studied radical anions are paired with Na$^+$ cations and the dianions are present in the form of disodium associates (cyclo-Alk^{2-},2Na$^+$).

The distinction between the cis and trans radical anions of stilbenes was demonstrated by the work of Ward et al.,[5] and even more conclusively by the spectral studies of Wang et al.[6] Ward et al.[5] showed also that the sodium salts of the stilbene dianions exist in THF in two forms, one referred to as "cis",

Table I

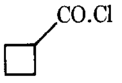
Carbon	δ ppm[a]	^{13}C-H coupling, Hz
^{13}C NMR Spectrum of 1,2-Diphenylcyclobutene in THF-d_8		
1 and 2	139.49	
3 and 4	27.28	^3J = 141.5
Ortho	129.02	^2J = 160.2
Meta	128.23	^2J = 158.5
Para	128.55	^2J = 160.6
Quaternary	137.06	
^{13}C NMR Spectrum of 1,2-Diphenylcyclopentene in $CDCl_3$		
1 and 2	138.2	
3 and 5	39.8	^3J = 130
4	22.7	^3J = 130
Ortho	128.9	^2J = 165
Meta	128.8	^2J = 164
Para	127.3	^2J = 164
Quaternary	139.1	
^{13}C NMR Spectrum of 1,2-Diphenylcyclohexene in THF-d_8		
1 and 2	135.8	
3 and 6	32.6	^3J = 130
4 and 5	24.0	^3J = 131
Ortho	129.7	^2J = 161
Meta	128.2	^2J = 163
Para	126.3	^2J = 164
Quaternary	144.9	

[a] The chemical shifts were determined from the decoupled spectra, relative to Me_4Si.

the other as "trans". The radical anions and dianions investigated in our study should be classified, therefore, as derivatives of *cis*-stilbene.

Purification and Identification of the Investigated Compounds. 1,2-Diphenylcyclobutene (B) was kindly provided by Dr. Charles D. DeBoer of the Eastman Kodak Co., whom we thank for his cooperation. This hydrocarbon was synthesized by Dr. T. Evans, who reduced dibenzoylethane with $LiAlH_4$ to the corresponding diol, converted the latter to the dichloro derivative, and finally cyclized it with $NaNH_2$ in liquid ammonia. The final product provided to us was chromatographed and crystallized from methanol. Before being used it was chromatographed again on an alumina column, eluted with petroleum ether, twice recrystallized from methanol, and then vacuum sublimed. Its ^{1}H NMR spectrum in deuterated THF showed a singlet at δ 2.72 accounting for four protons and two multiplets centered at δ 6.25 and 6.52 accounting for ten aromatic protons. The data deduced from its ^{13}C spectrum in deuterated THF are summarized in Table I. The assignment for carbons 3 and 4 is self-evident and confirmed by the observation of a direct coupling to two protons bonded to the pertinent carbon atoms and a weaker coupling to the adjacent two protons (^3J = 4.5 Hz). The relative intensity and a direct coupling to only one proton identifies the line of the para carbons, while the distinction between ortho and meta carbons is based on the observation of a strong coupling to one proton and additional weak coupling to only one proton (^2J = 7.5 Hz) for the former, but strong coupling to one proton and weak coupling to two protons (^3J = 7.4 Hz) for the latter. To differentiate between carbons 1 and 2 on one hand and the quaternary phenyl carbons on the other, we used a single proton frequency decoupling technique. Irradiation at the frequency of the aliphatic protons sharpened and increased the intensity of the 139.49 ppm line without affecting the 137.06 ppm line, while saturation at the frequency of aromatic protons led to a reverse result, sharpening the 137.06 ppm line without affecting the shape of the 139.49 ppm line.

Preparation of 1,2-diphenylcyclopentene, P, followed the procedure described in the literature.[7] Commercial acyl chloride I was converted into methyl ester II which yielded the diphenylcyclobutylcarbinol on addition of PhMgBr. On refluxing the latter in formic acid the rearrangement coupled with dehydration led to the formation of P.



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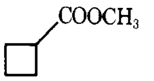


II

After being three times recrystallized from methanol, the produced hydrocarbon was satisfactorily pure, mp 59 °C. Its ^{1}H NMR in CCl_3D shows only one band centered at δ 7.11 for all the aromatic protons, a triplet at δ 2.90 (J = 7.3 Hz) attributed to the protons of the 3 and 5 methylene groups, and a quintet centered at δ 2.00 (J = 7.5 Hz) arising from the protons of the 4 methylene group. Integration of the spectrum led to results compatible with the proposed assignment.

The results derived from the ^{13}C NMR spectrum of P in CCl_3D are included in Table I. The lines attributed to carbons 3 and 5 and to carbon 4 are recognized by the magnitude of their chemical shifts and by their large splitting caused by coupling to two directly bonded protons. Their relative intensities and the effect of proton selective decoupling provided the base for their distinction. As in the NMR spectrum of B, the carbons 1 and 2 and the quaternary aromatic carbons absorb downfield of the other aromatic carbons; moreover, they are identified by their low intensity arising from long relaxation times and distinguished by the absence of any strong coupling to protons. Discrimination between these two lines is again based on the effect of proton selective decoupling. The remaining three lines of the proton-decoupled spectrum are attributed to the ortho, meta, and para carbons. The last one is distinguished by its lower intensity. All these lines are split into well-separated doublets by the single protons directly attached to these carbons. Closer examination of the long-range splitting allows us to ascribe the 128.9 ppm line to the ortho carbon and the 128.8 ppm line to the meta carbon.

Preparation and purification of 1,2-diphenylcyclohexene, H, was described previously.[8] The ^{1}H NMR spectrum in THF-d_8 shows an extremely narrow band centered at δ 7.96 accounting for all the aromatic protons. The two broader bands at δ 1.81 and 2.44 are due to the methylenic protons. Their assignment to the respective methylenic groups is based on the study of the ^{13}C NMR spectrum described below.

The results derived from the ^{13}C NMR are again collected in Table I. The magnitude of chemical shifts and the strong coupling to two directly attached protons proves that the lines at 24.0 and 32.6 ppm arise from the methylenic carbons. The ortho, meta, and para carbons are recognized by the magnitude of their chemical shifts, closely similar to those observed in the NMR spectra of B and P, and by their strong coupling to single, directly bonded protons. Their intensities and the examination of the long-range coupling (into doublet for the ortho carbons and triplet for the meta and para carbons) makes their assignment possible. The chemical shifts of the 1 and 2 carbons and of the quaternary aromatic carbons are again further downfield than those of the other aromatic carbons, and their low intensities provide further evidence for their identity.

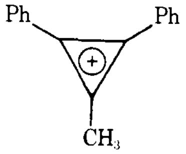
Selective proton decoupling of the aromatic protons sharpens the most downfield shifted 144.9 ppm line, and broadens the 135.8 ppm line, whereas decoupling of proton frequency of δ 2.44 line led to a reverse result, sharpening at 135.8 ppm and broadening at 144.9 ppm. This identifies the 144.9 ppm line as that of the quaternary phenyl carbons and the 135.8 ppm line as the quaternary olefinic carbons. Moreover, since the decoupling at the proton frequency of 2.44 ppm affected the olefinic, but not the quaternary, phenyl carbons, the corresponding proton band arises from the protons of the 3 and 6 methylenic group. Thus all the assignments of the proton and carbon lines are completed.

It is interesting to note that the large change in the chemical shifts of the olefinic and quaternary phenyl carbons is observed when the spectra of the cyclobutene and cyclopentene are compared with that of the cyclohexene. Namely, the olefinic carbons of the cyclohexene are shifted by about 2.5–3.5 ppm upfield from those of the corresponding carbons of the cyclobutene and pentene, whereas the quaternary phenyl carbons show the reverse shifts. It looks as though the charge is shifted from the rings into the olefinic bond when cyclohexene is replacing cyclobutene or pentene. Naively, one would expect, contrary to these observations, a similarity in the spectra of the cyclopentene and cyclohexene and larger deviations from them of the spectrum of the cyclobutene.

The mass spectra of B, P, and H show some common features. The molecular ion is the most abundant in the mass spectra of B and P; its relative abundance exceeds that of the *m/e* 91 (tropylium) ion by ~25% in the spectrum of B and even more, by a factor of ~3, in the spectrum of P. However, in the spectrum of H the molecular ion is ~3 times less abundant than the *m/e* 91 ion. The isotope lines are observed in all these spectra and their abundance conforms with the expectation.

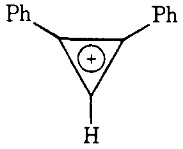
The relatively low abundance of the molecular ion in the spectrum of H is surprising. One would expect rather its low abundance in the spectrum of B.

In the mass spectra of all the three hydrocarbons an intense peak appears at *m/e* 205, and the structure



is attributed to the respective ion, although the loss of one hydrogen from B leading to the ion of an equivalent mass may also contribute to that peak in the mass spectrum of B. This seems to be justified by the exceptional intensity of that peak in the spectrum of B. A similar loss of H leads to a strong peak at *m/e* 219 in the mass spectrum of P.

Another common ion has *m/e* 191 and is attributed to



Finally, as expected, the ion *m/e* 178 attributed to diphenylacetylene appears in the mass spectra of all these hydrocarbons. Our findings are summarized in Table II, the relative abundances being given in percent of the abundance of the molecular ion.

Optical Spectra of 1,2-Diphenylcycloalkenes, Their Radical Anions and Dianions. The spectra of the hydrocarbons, B, P, and H, dissolved in ethereal solvents were recorded with a Beckman Acta IV spectrophotometer. In Table III we list the respective λ_{max} (a shoulder in the case of H) and the pertinent ϵ's.

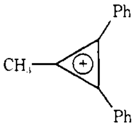
To record the spectra of the corresponding radical anions it was necessary to prepare their solutions virtually free of dianions. The degree of radical anions disproportionation is greatly reduced if hexamethylphosphoric triamide (HMPA) is used as a solvent. Therefore, an excess of the investigated cycloalkenes was dissolved in HMPA solutions of sodium biphenylide of known concentration. The electron transfer from the biphenylide to the cycloalkenes is quantitative as indicated by the disappearance of the absorbance of biphenylide. The disproportionation of the resulting free cycloalkene radical anions is negligible under these conditions; indeed the concentration of spins measured by the overmodulated ESR spectra recorded before and after the addition of the cycloalkene remains the same. Hence the concentration of the investigated radical anions was assumed to be that of the original biphenylide, and the molar absorbances given in Table III were calculated accordingly.

Our studies of equilibria and kinetics of disproportionation involved sodium ion pairs of the investigated radical anions in tetrahydrofuran (THF). A THF solution of $B^{-}\cdot,Na^{+}$ practically free of dianions could be prepared by reducing only a small fraction of B dissolved in that solvent. The spectrum of $B^{-}\cdot,Na^{+}$ in THF showed λ_{max} shifted toward shorter wavelength by 7 nm compared to that of the free $B^{-}\cdot$ in HMPA.

Table II. Mass Spectra of B, P, and H

	Rel abundance in percent of molecular ion		
m/e	B	P	H
234			100*
233			25 loss of H
221		20 isotope	
220		100*	
219		36 loss of H	
207	17 isotope		
206	100*	4	54 loss of C_2H_4
205[a]	70	23	73
204	13	9	29
203	15	8	41
202	11	7	39
192	7	12	39
191[b]	33	21	95
190	10	7	29
189	10	11	54
179	8	5	34
178[c]	22	11	83
177	5	2	20
176	10	4	34
165[d]	10	11	90
156			61
155			29
152[e]	7	6	56
143			98
129[f]	15	34	98
128	25	17	171
127	9	5	56
115[g]	19	75	220
91[h]	74	34	240

[a] Ion i. [b] Ion ii. [c] $PhC{\equiv}CPh^{+}$. [d] Fluorenyl^{+}. [e] Biphenylene^{+}. [f] Ion iii. [g] Ion iv. [h] Tropylium ion.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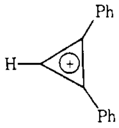
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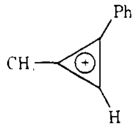
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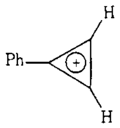
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Table III. Optical Spectra[a]

	Hydrocarbon		Radical anion		Dianion	
	λ, nm	$\epsilon \times 10^{-4}$	λ, nm	$\epsilon \times 10^{-4}$	λ, nm	$\epsilon \times 10^{-4}$
B	*297*	1.74	*500*	5.0	500	2.6
			530	1.2	*530*	3.0
			750	1.1		
P	*270*	1.10	500	1.7	*500*	2.9
			530	3.4	530	2.0
			750	0.9		
H	251 (s)	1.04			*358*	1.73
			470	0.7	*470*	2.34
			560	2.3	560	0.58

[a] The italicized wavelengths correspond to λ_{max}. The data obtained for the B system refer to THF solutions; those pertaining to $P^{-}\cdot$ and $H^{-}\cdot$ are obtained from their HMPA solutions.

Table IV. Disproportionation Equilibria in THF (Na^+ Counterion)

Cyclobutene (B)			
$10^3[B^{-}\cdot,Na^+]$, M	$10^3[B^{2-},2Na^+]$, M	$10^3[B]$, M	$K_{disp,B}$
2.7	0.2	2.3	0.1
2.7	0.4	2.1	0.2
2.8	0.5	1.9	0.1
2.4	1.6	1.2	0.3
2.4	2.6	0.2	0.1
		Av	0.16 ± 0.09

Cyclopentene (P)			
$10^5[P^{-}\cdot,Na^+]$, M	$10^5[P^{2-},2Na^+]$, M	$10^5[P]$, M	$K_{disp,P}$
1.40 (ESR)	4.65	42.5	104
1.25 (Spc)	4.75	42.5	129
1.90 (ESR)	12.8	33.5	107
2.00 (Spc)	12.8	33.5	110
5.50 (ESR)	46.6	76.9	118
5.35 (Spc)	46.7	76.9	125
6.00 (Spc)	5.20	70.9	103
5.25 (Spc)	6.85	55.0	138
		Av	118 ± 12

However, the molar absorbance was not affected by the change of solvent.

The disproportionation constants of $P^{-}\cdot,Na^+$ and $H^{-}\cdot,Na^+$ in THF are much larger than that of $B^{-}\cdot,Na^+$. Consequently their optical spectra in that solvent could not be investigated directly but the difference spectra of $2P^{-}\cdot,Na^+$ and $P^{2-},2Na^+$ and of $2H^{-}\cdot,Na^+$ and $H^{2-},2Na^+$ could be recorded by using flash-photolytic technique.[8] The λ_{max} of $P^{-}\cdot,Na^+$ and $H^{-}\cdot,Na^+$ in THF established by this technique agree with those observed in HMPA and the respective molar absorbances seem to be unaffected by the solvent. Note that the previously reported[8] ϵ (560 nm) of $H^{-}\cdot,Na^+$ is reduced to 2.3×10^4 after introducing a correction resulting from the absorbance of $H^{-}\cdot,Na^+$ at λ_{max} of $H^{2-},2Na^+$.

Exhaustive reduction on sodium mirror of B, P, and H in THF resulted in their quantitative conversion to the disodium salt of the respective dianions. The absence of radical anions in solutions derived from P or H was demonstrated by the lack of ESR signal. A minute ESR signal was noted in the solution of $B^{2-},2Na^+$. The ratio of two electrons to one cycloalkene in stoichiometry of the dianions was proved by their quantitative conversion to the radical anions of perylene or anthracene resulting from the addition of an excess of the pertinent aromatic hydrocarbon to their solution.

The spectroscopic data characterizing the dianions are collected in Table III. Its inspection reveals that λ_{max} of the dianions decreases with increasing ring size while a reverse trend is observed for the λ_{max} of radical anions.

Disproportionation Equilibria of the 1,2-Diphenylcycloalkenes Radical Anions. The equilibrated THF solutions of the cycloalkenes and of sodium salts of their radical anions and dianions were prepared and studied at ambient temperature. The equilibria are described by the equations

$$2B^{-}\cdot \text{ (or } P^{-}\cdot\text{, or } H^{-}\cdot\text{)},Na^+ \rightleftarrows B \text{ (or P or H)} + B^{2-} \text{ (or } P^{2-} \text{ or } H^{2-}\text{)},2Na^+ \quad (1)$$

i.e., K_{disp} = [hydrocarbon][dianion salt]/[radical anion salt]^2.

In studies of the B system the concentrations of $B^{-}\cdot,Na^+$ and $B^{2-},2Na^+$ were obtained by spectrophotometry using the ϵ's listed in Table III. The concentration of the unreduced hydrocarbon was obtained by subtracting $[B^{-}\cdot,Na^+] + [B^{2-},2Na^+]$ from the initial concentration of B. The results are summarized in Table IV. The average value of $K_{disp,B}$ is 0.16 ± 0.09 and its relatively low value explains why THF solutions of $B^{-}\cdot,Na^+$ with a negligible contamination of $B^{2-},2Na^+$ could be prepared.

In the investigation of the P system the concentration of P^{2-}, $2Na^+$ was determined spectrophotometrically whereas overmodulated ESR spectra and spectrophotometry were utilized in determining $[P^{-}\cdot,Na^+]$. The concentration of the unreduced P was again calculated from the material balance. These results are also summarized in Table IV and the average $K_{disp,P}$ is found to be 118 ± 12.

The disproportionation constant of $H^{-}\cdot,Na^+$ in THF was reported earlier.[8] Our present results agree with the previous one leading to $K_{disp,H}$ of about 3000 if the corrected ϵ's are used in computation.

Kinetics of Disproportionation of 1,2-Diphenylcycloalkene$^{-}\cdot$,Na$^+$ in THF. The flash-photolytic technique described in previous publications[1b,c,3,8] was utilized also in the present investigation. Flash of visible light leads to electron photoejection from the cycloalkene radical anions or dianions present in an equilibrated solution of the pertinent hydrocarbon and the sodium salts of its radical anions and dianions. Depending on the system and its composition two events may be observed after a flash:

(a) Most of the photoejected electrons come from radical anions and are captured by the unphotolyzed radical anions. As a result the concentration of radical anions decreases after a flash and the concentration of the unreduced hydrocarbon and of its dianion increases accordingly. For example,

$$B^{-}\cdot,Na^+ \xrightarrow{h\nu} B + e^{-},Na^+ \qquad (2)$$

$$B^{-}\cdot,Na^+ + e^{-},Na^+ \rightarrow B^{2-},2Na^+ \qquad (3)$$

In the dark period following the flash the equilibrium is reestablished, i.e.,

$$2B^{-}\cdot,Na^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + B^{2-},2Na^+ \qquad (4)$$

and the course of this relaxation may be followed by monitoring the decrease in the absorbance of the dianions or bleaching of the radical anions.

(b) When the perturbation of the equilibrium results from electron ejection from the dianions and electron capture by the unreduced hydrocarbon, their concentrations decrease after a flash while the concentration of radical anions increases. The relaxation of the system to its original state of equilibrium is described by the same equation as stated above, but the bleaching would appear where the dianions absorb and the absorbance at λ_{max} of radical anions would increase.

In either case the kinetics of the relaxation is given by a linear relation $\ln [(a + bx)/x] = \text{const} + \frac{1}{2}ak_{-1}t$, where $a = 4K_{dispr}\,[\text{radical anion}]_e + [\text{dianion}]_e + [\text{hydrocarbon}]_e$ and $b = 4K_{dispr} - 1$. The subscript e refers to the equilibrium concentrations of the reagents which are determined spectrophotometrically from the absorbance of the photolyzed solution before a flash or long after a flash, both spectra being identical indicating the absence of irreversible reactions. The concentration of hydrocarbon is calculated using the determined K_{dispr}. Symbol x denotes the excess (or its depletion) of radical anions concentration at time t.

Most of the experiments were performed in a 10-cm long cylindrical cell, the concentrations of the reagents being at about 10^{-6} M, but a few runs were performed in a 1-cm cell at approximately 10 times higher concentrations of the reagents. To avoid problems resulting from the ionic dissociation of ion pairs, the photolyzed solutions were buffered with $NaBPh_4$. The details of the technique were described elsewhere.[1b,c,9]

The results of our studies are summarized in Table V. In the cyclobutene system a flash led to bleaching of $B^{-}\cdot,Na^+$ and

Table V, Kinetics of Disproportionation of Sodium Salts of Radical Anions of 1,2-Dicycloalkenes in THF at Ambient Temperature

$$2B^{-}\cdot(P^{-}\cdot \text{ or } H^{-}\cdot),Na^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B(P \text{ or } H) + B^{2-}(P^{2-} \text{ or } H^{2-}),2Na^{+}$$

System $B^{-}\cdot,Na^{+}$ (formation of $Bu^{2-},2Na^{+}$)

10^7[B], M	$10^7[B^{-}\cdot,Na^{+}]$, M	$10^7[B^{2-}$, $2Na^{+}]$, M	λ, nm, of monitoring light	$10^{-8}k_{-1}$, ms
47.	137.	60.[a]	500 (b)	1.4
47.	137.	60.[a]	540 (a)	1.4
7.6	19.0	7.3	500 (b)	1.6
7.6	19.0	7.3	540 (a)	1.9
8.0	17.0	5.0	500 (a)	2.0
5.7	11.0	3.1	500 (a)	1.3

Av $k_{-1} = (1.6 \pm 0.3) \times 10^8$ M^{-1} s^{-1}

$k_1 = (2.4 \pm 0.3) \times 10^7$ M^{-1} s^{-1}

System $P^{-}\cdot,Na^{+}$ (formation of $P^{-}\cdot,Na^{+}$)

10^6[P], M	$10^6[P^{-}\cdot,Na^{+}]$, M	$10^6[P^{2-}$, $2Na^{+}]$	λ, nm, of monitoring light	$10^{-5}k_{-1}$, ms
22.0	1.00	5.0	530 (a)	3.7
22.0	1.00	5.0	750 (a)	3.7
32.5	1.81	11.1[a]	530 (a)	4.3
32.5	1.81	11.1[a]	750 (a)	4.1
311.	7.43	19.5[a]	530 (a)	2.3
311.	7.43	19.5[a]	750 (a)	2.1
179.	7.42	33.9[a]	530 (a)	4.6
179.	7.42	33.9[a]	750 (a)	3.6
22.3	1.08	5.8	530 (a)	3.4
22.3	1.08	5.8	750 (a)	2.8

Av $k_{-1} = (3.5 \pm 0.8) \times 10^5$ M^{-1} s^{-1}

$k_1 = (3.8 \pm 0.8) \times 10^7$ M^{-1} s^{-1}

System $H^{-}\cdot,Na^{+}$ (bleaching $H^{2-},2Na^{+}$)

10^6[H], M	$10^6[H^{-}\cdot,Na^{+}]$, M	$10^6[H^{2-}$, $2Na^{+}]$, M	λ, nm, of monitoring light	$10^{-8}k_1$, ms
5.7	Undetectable	2.5	470 (b)	0.8
5.7	Undetectable	2.5	560 (a)	1.0

$k_{-1} \approx 3 \times 10^4$ M^{-1} s^{-1}

$k_1 = 9 \times 10^7$ M^{-1} s^{-1}

[a] 1-cm cell. (a), absorbance; (b), bleaching.

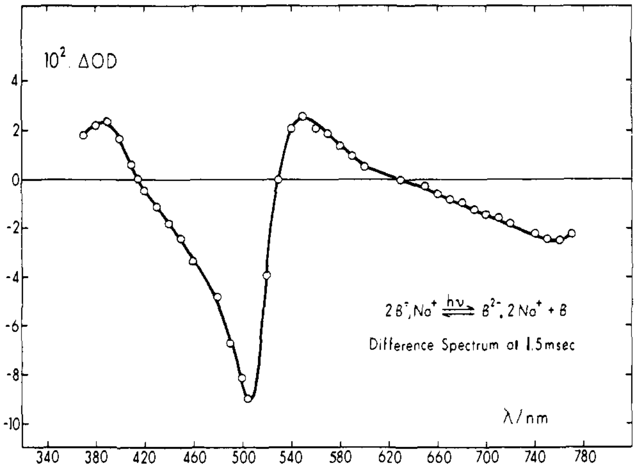

Figure 1. The difference spectrum recorded in flash photolysis of $B^{-}\cdot,Na^{+}$ at 1.5 ms after flash.

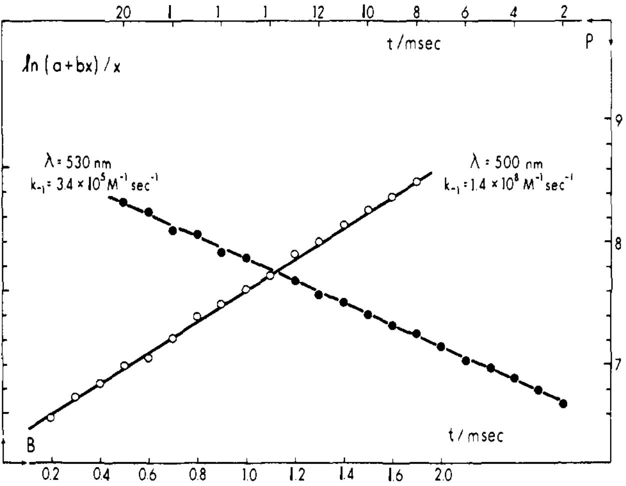

Figure 2. Kinetic results obtained in the flash photolysis of radical anions–dianions mixture. Open circles—the butene system, left and bottom scale; full circles—the pentene system, right and upper scale.

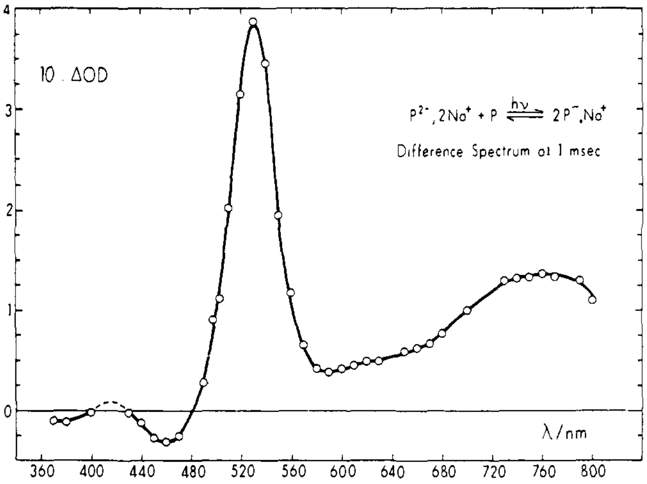

Figure 3. The difference spectrum recorded in flash photolysis of $P^{-}\cdot,Na^{+}$ at 1 ms after flash.

formation of $B^{2-},2Na^{+}$. This is clearly seen in Figure 1 showing the difference spectrum of a photolyzed solution at 1.5 ms after a flash. The shape of this spectrum for λ > 440 nm agrees with the Beckman recorded absorbance spectrum of $B^{2-},2Na^{+}$ from which one subtracts the absorbance spectrum of $B^{-}\cdot,Na^{+}$ at concentration twice as high as that of $B^{2-},2Na^{+}$. Particularly, the appearance of the two isosbestic points at 530 and 625 nm is significant; their position agrees with that predicted from the constructed difference spectrum based on Beckman data, this proving that indeed two $B^{-}\cdot,Na^{+}$'s are destroyed as one $B^{2-},2Na^{+}$ is formed.

A typical plot of ln $[(a + bx)/x]$ vs. time is shown in Figure 2, and from the slopes of such lines we calculated the k_{-1} values given in the last column of Table V.

A transient absorbance appearing in Figure 1 at 390 nm has not been identified yet. It represents some species that does not participate in the studied disproportionation and that decays much faster than the 500 and 540 transients.

The difference spectrum recorded in a flashed solution of $P^{-}\cdot,Na^{+}$ is shown in Figure 3. Its shape corresponds to the constructed spectrum of $P^{-}\cdot,Na^{+}$ from which a spectrum of $P^{2-},2Na^{+}$ (at half concentration of the former) is subtracted. The calculated isosbestic point at 487 nm agrees with the observed one. Hence, electrons photoejected from $P^{2-},2Na^{+}$ are captured by P leading to increase in the concentration of $P^{-}\cdot,Na^{+}$. A typical plot of ln $[(a + bx)/x]$ vs. time obtained in these experiments is included in Figure 2.

The kinetics of disproportionation of $H^{-}\cdot,Na^{+}$ was reported earlier.[8] In this system hardly any radical anions are present at equilibrium, and hence we observe after a flash a simple bimolecular reaction,

$$2H^{-}\cdot,Na^{+} \xrightarrow{k_1} H + H^{2-},2Na^{+} \qquad (5)$$

i.e., a plot of $1/x$ vs. time is linear, its slope giving k_1 ($\Delta\epsilon$). Two experiments were performed and the results, included in Table V, agree with those previously reported.[8]

Using the disproportionation constants discussed in the preceding section we calculated k_1 for the $B^{-}\cdot,Na^{+}$ and $P^{-}\cdot,Na^{+}$ system and k_{-1} for the $H^{-}\cdot,Na^{+}$ system. All these data are given in Table V.

Discussion

The following ramifications emerge from our results pertaining to THF solutions of sodium salts of radical anions derived from 1,2-diphenylcyclobutene, -pentene, and -hexene. The disproportionation constants increase with increasing size of the ring, being 0.15, 110, and about 3000 for the four-, five-, and six-membered rings, respectively. The tighter association of the cations with the dianion, when compared with the cation-radical anions pairing, is an important factor driving the disproportionation,[3a,4] and this effect might be invoked in explaining the above results. For example, the structure of the Na^{+} radical anion pairs could become looser as the ring increases, whereas the same structural changes would make the Na^{+},dianion,Na^{+} aggregates tighter. Although such an explanation could gain support from the spectral observations[25] summarized in Table III, it is conceptually unsatisfactory—why would the variation in the ring size affect in reverse direction the cation–anion interaction in radical anion pairs and in dianion aggregates? Alternatively, we may claim that some strain in the radical anions is released or reduced on their conversion to dianions. This approach seems presently to be more satisfactory and will be elaborated further.

Before pursuing the above argument let us stress that the disproportionation rate constants, k_1's, are only slightly affected by the size of the ring; they are 2.4×10^{7}, 3.8×10^{7}, and $\sim 9 \times 10^{7}$ M^{-1} s^{-1} for the -butene, -pentene, and -hexene, respectively. Their high values and a virtual lack of the ring effect seem to indicate that the transition states of these disproportionations lie only slightly above the respective initial state. Their structures correspond most probably to a linear array $A^{-}\cdot,Na^{+},A^{-}\cdot,Na^{+}$ in which some THF molecules externally solvating the Na^{+} cations become partially or completely released. Such a transition state would be hardly affected by the variation of the size of the ring. Of course, the rates of the reverse reactions, the formation of radical anions from dianions and parent hydrocarbons, must then reflect the changes in K_{dispr}; thus their rate constants, k_{-1}, decrease from 1.6×10^{8} M^{-1} s^{-1} for the butene system to 3.5×10^{5} M^{-1} s^{-1} for the pentene and to $\sim 3 \times 10^{4}$ M^{-1} s^{-1} for the hexene.

Consideration of the disproportionation of the *cis*- and *trans*-stilbenide radical anions should be helpful in any attempt at clarifying the above discussed relations. As is known, *trans*-stilbene is thermodynamically more stable than its cis isomer. Although the room temperature value of the equilibrium constant, K_{CT}

cis-stilbene ⇄ *trans*-stilbene, K_{CT}

is not exactly known, undoubtedly it is greater than 100. The lower stability of the cis isomer is attributed to the steric hindrance arising between the two phenyl groups placed in cis position. The thermochemical data derived from the heats of hydrogenation of the stilbenes,[10] or their heats of combustion,[11,12] lead to $\Delta\Delta H_f$ for the gaseous hydrocarbon of at least 4 kcal/mol and more probably 6 kcal/mol. Provided that only $\Delta\Delta H_f$ determined K_{CT}, its value is expected to be $\sim 10^{3}$.

Redox potentials of both isomers are similar. The equilibrium constant of the electron transfer, K_{tr},

cis-stilbenide$^{-}\cdot$,Na^{+} + *trans*-stilbene ⇄ *cis*-stilbene + *trans*-stilbenide$^{-}\cdot$,Na^{+}

was determined[6] at about 5, and similar values were deduced for the transfer between the free ions.[13,14] Apparently reduction of *cis*-stilbene to its radical anion does not release the steric strain operating in the hydrocarbon, and hence the equilibrium constant, $K_{C^{-}\cdot,T^{-}\cdot}$

cis-stilbenide$^{-}\cdot$,Na^{+} ⇄ *trans*-stilbenide$^{-}\cdot$,Na^{+}, $K_{C^{-}\cdot,T^{-}\cdot}$

is again large, viz., $K_{C^{-}\cdot,T^{-}\cdot} = K_{tr} \cdot K_{C,T} > K_{C,T}$.

The disproportionation constant of the sodium salt of *trans*-stilbenide in THF was estimated by Garst[15] at $\sim 10^{-3}$, and our recent potentiometric study[16] leads to a value of ~ 0.03 at ambient temperature. The data of Ward et al.[5] allow us to calculate the disproportionation constant of sodium *cis*-stilbenide in THF as 250. Its largeness, when compared with $K_{\mathrm{dispr},T^{-}\cdot,Na^{+}}$, is significant. It suggests that the strain operating in *cis*-stilbene and in its radical anion is alleviated in the dianion. Since

$$K_{\mathrm{dispr},T^{-}\cdot,Na^{+}}/K_{\mathrm{dispr},C^{-}\cdot,Na^{+}} = [K_{C,T}/(K_{C^{-}\cdot,T^{-}\cdot})^{2}]K_{C^{2-},T^{2-}} = K_{C^{2-},T^{2-}}/K_{tr}{}^{2} \cdot K_{C,T}$$

the above data yield a value for $K_{C^{2-},T^{2-}}$, the equilibrium constant of the conversion

cis-stilbene^{2-},$2Na^{+}$ ⇄ *trans*-stilbene^{2-},$2Na^{+}$

of the order of unity. The stabilities of the dianions are comparable while both the cis hydrocarbon and its radical anion are much less stable than the respective trans isomers. In fact, the results of Wang et al.[6] suggest that the reduction of the free stilbenide radical anions yield only one kind of free dianions. It seems that change of shape makes dianions strain free, while the strain reduces the stability of *cis*-stilbene and its radical-anion.

This discussion raises a question. What are the shapes of the stilbenes, their radical anions and dianions? X-ray studies of crystals of *trans*-stilbene were interpreted by Robertson and Woodward[17] in terms of a planar molecule of C_i symmetry. Recent refinements[18] essentially confirm this conclusion, although a slight deviation from planarity, i.e., a twist of the phenyl groups by 3–6° out of the C=C plane, has not been excluded. However, electron diffraction study of the gaseous *trans*-stilbene, jointly reported in 1975 by two independently working groups,[19] led to astonishing results. According to these authors the molecule of *trans*-stilbene in the gas phase has a propeller-like shape with C_2 symmetry. The C–Ph dihedral angles were claimed to be ~30° provided that the C=C bond is not twisted, and ~20° if the C=C bond is twisted by 10°—a likely conformation according to these workers. These surprising observations call for explanation.

The geometry of *cis*-stilbene was deduced from the electron-diffraction study by Traetteberg and Frantsen.[20] The molecule is again claimed to be propeller-like with C_2 symmetry but the C–Ph dihedral angles appear to be much larger than in the trans isomer, namely, about 43°. The steric strain is claimed to be revealed by the large C=C–C angle of 129.7° (0.7), but comparable angles were reported for the apparently unstrained trans isomer, namely, 130 (ref 17), 126 (ref 18), and 127.7° (ref 19).

No published information is available pertaining to the shape of radical anions. However, a recent report[21] described the shape of the *trans*-stilbene dianion deduced by Stucky[21] from his x-ray studies of crystals of the dilithium salt complexed with TMEDA or PMDTA. The stilbene moiety appears to be planar in both complexes; the lithium ions seem to be located below and above the plane at a distance of 2.03 A from the center of the C=C bond. A conflict with the conclusions derived from the electron diffraction work[19] is apparent. Greater deviation from the planarity could be expected in the dianion than in the hydrocarbon, and indeed Garst et al.,[22] following the arguments forwarded by Walsh[23] and by Pearson,[24] anticipated a skewed structure for the dianion.

The findings reported in the literature are obviously confusing. We believe, however, that the *trans*-stilbene dianion, if associated with its counterions, acquires a planar shape, or slightly distorted from planarity. Of course, such a distortion would be appreciable in the cis dianion and it could release the strain. The kinetic data of Ward et al.[5] conclusively demonstrate the existence of two distinct kinds of stilbene dianion salts—a conclusion that hardly could be reconciled with a fully skewed structure even if a distinction between different placements of cations is contemplated. It is probable, on the other hand, that the free dianions, not associated with the counterions, acquire a fully skewed shape, and then no distinction could be made between those derived from the cis or trans isomers.

Our findings concerned with the disproportionation of radical anions of 1,2-diphenylcycloalkenes may be rationalized in terms of the arguments outlined here. Apparently the strain operating in the radical anions of the diphenylcyclopentene and -hexene are released on their reduction. The strain might be enhanced by the constraints of the ring accounting thus for the higher tendency for disproportionation in the cyclohexene system. The large C=C–C angles in the diphenylcyclobutene may decrease the strain in its radical anions and thus reduce their tendency for disproportion.

The deviation from planarity may affect the electron densities in the C=C bond and such an effect, operating in the appropriate direction, could enhance the disproportionation by increasing the cation–anion interaction in the dianions. However, no tangible evidence to substantiate this idea is available. The charge density on the central carbons of *trans*-stilbene dianions is apparently higher than anticipated from the simple Hückel treatment, and this may justify the relatively high disproportionation of salts of the respective radical anions.

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