The Nuclear Magnetic Resonance Spectra of Cyclic 1,3-Diphenylallyl Cations. Some Observations on 1,3-Orbital Interaction^{1a}

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The possibility of 1,3-orbital overlap stabilization in the 1,3-diphenylcyclobutenyl cation (3) is explored by comparison of the nmr spectra of cycloalkenyl cations 1-4. It is concluded that 1,3-electrostatic repulsion results in charge dispersion in cation 3. Extensive charge dispersion onto the phenyls in diphenylcyclopropenium ion (4) is found, accompanied by an unusually low barrier to rotation in accord with extended Hückel calculations. Several useful syntheses of cyclobutane and cyclobutene derivatives are described.

PhCOCH₂CO₂C₂H₅

In some earlier papers we suggested that the paraproton resonance of phenyl-substituted carbonium ions was a reasonable quantitative measure of the stability or electron demands of the carbonium ion center.² We had hoped to use this method to look for stabilization by 1,3-orbital overlap in the series of allyl cations: 1,3diphenylcyclohexenyl (1), 1,3-diphenylcyclopentenyl (2), 1,3-diphenylcyclobutenyl (3), and 1,3-diphenylcyclopropenyl (4) cations. Normally, if there were stabil-



ization of the cations by 1,3 overlap, one would expect the stabilization to increase as ring size decreased. One would therefore expect the para-proton resonance of the phenyl substituents on these cations to move upfield as one moved to smaller and smaller ring sizes. Although we have since shown that the para-proton resonance is in fact a very insensitive measure of carbonium ion stability,^{2b} and Taft has shown that the fluorine resonance is orders of magnitude more sensitive,³ we nonetheless believe that the unexpected results of our investigation of the cyclic allyl cations, as well as some interesting synthetic methods developed in their preparation, warrant publication at this time.

The diphenylcyclopropenium ion (4), has, of course, been known for some time.^{4,5} The diphenylcyclohexenyl (1) and diphenylcyclopentenyl (2) cations were prepared by solution of the corresponding dienes in cold fluorosulfonic acid. The dienes were synthesized in an unexceptional way as indicated in Scheme I.

The attempted synthesis of 1,3-diphenylcyclobutenyl cation caused unexpected aggravation but was finally accomplished as indicated in Scheme II.

Several points in Scheme II deserve comment. The first step, photodimerization of β -nitrostyrene, has been

(4) D. G. Fallaum and M. Bull, *ibid.*, **62**, 2651 (1960).
 (5) R. Breslow and H. Höver, *ibid.*, **82**, 2644 (1960).



SCHEME I

CH2=CHCOCH3

PhCH₂N⁺(CH₃)₃

reported in the literature.⁶ The reaction, however, was conducted on solid material by spreading a thin film of

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^{(2) (}a) D. G. Farnum, J. Amer. Chem. Soc., 89, 2970 (1967); (b) D. G. Farnum and G. Mehta, *ibid.*, 91, 3256 (1969).

 ⁽³⁾ R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965).
 (4) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

⁽⁶⁾ R. D. Campbell and R. F. Ostead, Proc. Iowa Acad. Sci., 71, 197 (1964).

TABLE	I
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Chemical Shifts for 1,3-Diphenylcycloalkenyl Cations ($ au$ Values)							
Cation	Ortho H	Meta H	Para H	Methine H	Other H		
Cylcohexenyl 1	1.77	2.41	2.14	1.46	6.42 (4 H) 7.64 (2 H)		
Cyclopentenyl 2	1.76	2.35	2.10	1.51	6.04		
Cyclobutenyl 3 Cyclopropenyl 4	$\begin{array}{c} 1.75\\ 1.55\end{array}$	$\begin{array}{c} 2.18 \\ 2.10 \end{array}$	$\begin{array}{c} 1.98 \\ 1.92 \end{array}$	1.87 - 0.45	5.82		

the crystals at the bottom of a crystallizing dish and irradiating this film with occasional stirring over a period of several days or weeks. We find that the yield and quantity of material obtained in this reaction can be markedly enhanced by the simple expedient of conducting the reaction in a vigorously stirred concentrated slurry of the finely powdered crystals in water suspension. This technique has also been applied to the photodimerization of cinnamic acid and will be described elsewhere.⁷ The second step in the sequence, reductive methylation of dimer 5 (X = NO_2) to give 5 [X = $N(CH_3)_2$], was originally accomplished in the usual twostep method. That is, the nitro groups were first reduced with zinc and acetic acid and the resulting unstable diamine was then methylated with formaldehyde and formic acid. The modified one-step procedure, involving reduction of the nitro groups with zinc and formic acid, and concomitant reductive methylation of the resulting diamine with formaldehyde works extremely well. The method gives high yields in a convenient procedure and may be a general method for the conversion of nitro compounds to dimethylamino compounds. The final step in the synthesis, the conversion of the dibromocyclobutane $\mathbf{6}$ to the methoxycyclobutene 7 (X = OCH₃) is an interesting example of the competition between dehydrobromination and nucleophilic displacement on the dibromide. The reaction conditions are apparently quite critical and took some time to work out. Several methods for this type of conversion were attempted, including a variety of bases in methanolic solution and dimethyl sulfoxide (DMSO) solution, a variety of nucleophiles in different solvent systems, and sulfuric acid, fluorosulfonic acid, and a mixture of fluorosulfonic acid and antimony pentafluoride. Only the reagent indicated in Scheme II, potassium iodide in DMSO with a limited amount of methanol, proved to be successful. One other reagent combination, sodium cyanide in acetonitrile-DMSO, was found to give a related reaction-conversion of dibromide 6 to the cyclobutenyl cyanide 7 (X = CN). However, we could not convert the product to the cyclobutenyl cation 3, nor could we hydrolyze it to the carboxylic acid 7 (X = $CO_{2}H$), although we were able to obtain the amide 7 $(X = CONH_2)$ from the cyanide 7 (X = CN) with sodium methoxide in DMSO (see Scheme II).

An alternative four-step synthesis of trans-1,3-diphenylcyclobutane (5, X = H) in about 20% overall yield from α -trans-cinnamic acid was also developed and is diagrammed in Scheme III.

All of the 1,3-diphenylcycloallyl cations thus prepared were stable in fluorosulfonic acid at room temperature, although the cyclobutenyl and cyclopropenyl cations could be kept much longer than the other two without deterioration. The structures of the cations

SCHEME III

PhCH=CHCO₂H
$$\xrightarrow{h_{\nu}}$$
 5, X = CO₂H (60%) $\xrightarrow{\text{SOCl}_2}$
5, X = COCl (80%) $\xrightarrow{(CH_3)_3\text{COOH}}$
5, X = CO₃C(CH₃)₃ (80%) $\xrightarrow{p\text{-cymene}}$ 5, X = H (50%)

were confirmed both by their nmr spectra and also by quenching the cations to give the starting dienes or ethers with sodium methoxide in methanol.

The chemical shifts of the para protons in the several cations were determined as we described previously.^{2a} τ values for the several key protons in the cations are given in Table I. Note that, although the differences are small, the τ values for the para protons fall in the reverse order from that expected for increasing 1,3-overlap stabilization with decreasing ring size. This fact is particularly surprising for the 1,3-diphenylcyclopropenium ion, for which we know there is large delocalization stabilization in the cyclopropenium ion, and for which we expect, therefore, much less charge dispersion onto the attached phenyl rings.^{8,9} The meta-proton chemical shifts parallel the para shifts and are slightly larger, in accord with an *inductive* dispersal of charge to the attached phenyl. The ortho- and methine-proton chemical shifts are much less susceptible to reliable interpretation because of the proximity of the magnetically anisotropic phenyl and allyl cation systems and the different geometries of the cations.^{2a,9} However, the dramatic low-field shift of the cyclopropenium ion ortho and methine protons must reflect the ring current effect of this 2- π -electron system.^{4,5,8,9}

We can suggest two factors which were ignored in our original expectations and which could conspire to produce the unexpected results which we observe. The first factor is the electrostatic repulsion engendered by bringing the two ends of the allyl system, each with about one-half a positive charge, closer together in the small ring system. This repulsion would be a destabilizing factor and would cause the positive charge to disperse onto the phenyl rings. Such inductive charge dispersal would also be in accord with the larger downfield shift of the meta than para protons with decreasing ring size.

We suggest the second factor in order to account at least in part for the anomalous low-field shift of the para proton in diphenylcyclopropenium ion. In comparing this ion with the cyclobutenyl cation, we have replaced the alkyl substituents on the cyclobutenyl cation, that is, the ring methylene group, by a direct bond between the trigonal carbon atoms in the system. We have therefore lost the large inductive stabilizing effect of the methylene group. In other words, we suggest that the

⁽⁷⁾ D. G. Farnum and A. Mostashari, "Photochemical Syntheses," R. Srinivasan, Ed., in press.

⁽⁸⁾ R. Breslow, H. Hover, and H. W. Chang, J. Amer. Chem. Soc., 84, 3168 (1962).

⁽⁹⁾ D. G. Farnum and C. F. Wilcox, ibid., 89, 5379 (1967).

cyclopropenyl cation is not a good system for comparison with the cyclobutenyl cation because it is less substituted. In fact, it is difficult to see how one could obtain a good model for the cyclopropenyl cation. We have tried to prepare the unsubstituted 1,3-diphenylallyl cation as a compromise model but find that under our conditions this cation cyclizes much too rapidly to enable its nmr spectrum to be determined.

An interesting point emerges from observation of the variable temperature nmr spectra of cations 1-4. Thus the cyclohexenvl and cyclopentenvl cations 1 and 2 give essentially no change in the nmr other than viscosity broadening down to -50° . In particular, the four ortho protons seem to remain equivalent appearing as a doublet of doublets, indicating essentially free rotation about the C-phenyl bonds on an nmr time scale for these cations. In contrast, the nmr spectrum of cyclobutenyl cation 3 begins a reversible broadening of the ortho-proton doublet of doublets as the temperature is lowered to 0° . Below -40° the spectrum sharpens again with two ortho protons appearing as a broad lowfield doublet at τ 1.46 and the remaining two ortho protons lost in the higher field 9-proton multiplet. Thus there is onset of restricted rotation in cation 3 near 0° . The higher barrier to rotation in cation 3 than in cations 1 and 2 is in complete accord with the observed greater dispersal of charge to the phenyl groups in cation 3, and contrary to expectations based on steric grounds.

On the basis of the preceding arguments and observations alone, cyclopropenium ion 4 would be expected to exhibit restricted rotation at a temperature higher than 0° , since its para-proton resonance indicates still more dispersal of positive charge onto the phenyl groups than in 3. Therefore, the observation of equivalence of ortho protons in the nmr of cyclopropenium ion 4 down to -50° is especially surprising. However, a low barrier to rotation, nonetheless accompanied by significant charge dispersal onto the phenyl groups, is exactly what has been predicted for the cation 4 on the basis of extended Hückel calculations.¹⁰ Our observation provides a convincing test of this suggestion.

We conclude, then, that these results suggest that a 1,3-electrostatic repulsive interaction in the cyclobutenyl cation must also be considered as a contributer to destabilization and charge dispersion in the cation. This effect may be superimposed upon a 1.3-attractive or -bonding interaction which makes its contribution to stabilization and charge dispersion in the cations. We have no way at present of telling which of these two factors, the destabilizing or stabilizing, is more important in the 1,3-diphenylcyclobutenyl cation 3. We also conclude that the diphenylcyclopropenium ion 4 exhibits an unusually low barrier to rotation about the C-phenyl bonds inconsistent with intuitive expectations based upon the extent of positive charge dispersal onto the phenyl groups but consistent with extended Hückel calculations.10

Experimental Section

are recorded in τ values relative to tetramethylsilane internal standard unless otherwise indicated. The following format is used: τ value (multiplicity, coupling constant values, number of H's) with the following abbreviations, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Determination of Nmr Spectra of the Carbonium Ions. Solutions of the carbonium ions for nmr study were prepared by dissolving the appropriate precursor in a small amount of Freon 114B and adding the solution dropwise to stirred fluorosulfonic acid maintained at Dry Ice-acetone bath temperature. Solutions were made up to 5-10% precursor, and a small amount of tetramethylammonium fluoroborate (τ 6.87²) was added as internal reference when needed. For recovery studies, solutions were quenched by pouring slowly into excess sodium methoxide in methanol at ice bath temperatures. Products were then isolated by extraction with pentane after swamping with water. The pentane extracts were dried over magnesium sulfate and evaporated to dryness. The residues were compared spectroscopically (nmr, ir) with starting materials and found to be virtually identical in every case.

3-Phenylcyclopent-2-enone. A. Condensation.—Ethyl aceto-acetate (26 g, 0.2 mol) in dry benzene (250 ml) was added to sodium hydride (9.6 g of 50% dispersion in oil) in benzene with stirring under a nitrogen atmosphere. After the completion of the reaction (indicated by cessation of bubbling of hydrogen), phenacyl bromide (40 g, 0.20 mol) was added at once and the mixture was refluxed for 6 hr. The reaction mixture was then washed with cold water twice (total of 800 ml). The benzene solution was dried over magnesium sulfate and evaporated to give an oil, the nmr spectrum of which exhibited peaks characteristic of ethyl benzoylpropionate and 1-phenyl-3-carbethoxypentane-1,4-dione.

B. Saponification and Decarboxylation.-The product of the above reaction was placed in a 3-1. flask, an 0.8% solution of potassium hydroxide (2.5 1.) was added, and the mixture was refluxed under a nitrogen atmosphere for 2.5 hr. The reaction mixture was then cooled and extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. Evaporation of the ether gave a brownish oil which was chromatographed over alumina. The diketone (1-phenylpentane-1,4-dione) $(\bar{7} g)$ was eluted first with ethyl acetate-benzene (20:80). A mixture of the diketone and 3-phenylcyclopent-2enone (7.5 g) followed by the cyclopentenone (4.5 g) was eluted with ethyl acetate. The diketone was separated from the mixture by distillation: bp 104° (0.35 mm); ir (neat) 1720, 1695 cm⁻¹; nmr (CCl₄) τ 2.2 (m, 2 H), 2.68 (m, 3 H), 7.16 (A₂B₂, q, 4 H), 7.97 (s, 3 H). 3-Phenylcyclopent-2-enone (2 g) was obtained from the residue by crystallization from hexane-ether.

C. Ring Closure.-The combined diketone crop (12 g) was refluxed in aqueous potassium hydroxide (250 ml of a 10% solution) under a nitrogen atmosphere for 2 hr to give 9.5 g of a light brownish phenylcyclopentenone isolated by chromatography as above, giving a total overall yield of 52%. The pure ketone was obtained by sublimation of the crude product: mp 83.5-84.5° (lit.¹¹ 83–84°); ir (CCl₄) 1705–1695 cm⁻¹; nmr (CDCl₂) τ 2.6 (m, 5 H), 3.6 (t, J = 1.5 cps, 1 H), 7.05 (m, 2 H), 7.55 (m, 2 H).

1, 4-Diphenyl-1, 3-cyclopenta diene. - 3-Phenyl cyclopente none(3.16 g, 0.02 mol) in ether (20 ml) was added to phenyl Grignard reagent prepared from bromobenzene (3.3 g, 0.021 mol) and magnesium turnings (50 mg) in ether under an argon atmosphere. After 3 hr the reaction was worked up by adding concentrated animonium chloride solution. The ether solution was washed with water and evaporated to give an oil, which was dissolved in methanol with warming. When the methanolic solution was chilled, 2.9 g (35%) of solid was obtained: mp 155.5-157° (lit.¹² 155-157°); mmr (CDCl_b) τ 2.6 (m, 10 H), 3.12 (t, J = 1cps, 2 H), 6.27 (t, J = 1 cps, 2 H).

3-Phenylcyclohex-2-enone. A. Michael Condensation.-This reaction was done according to Walker.13 A 40% methanol solution of Triton B (60 ml) was added with stirring to a solution of ethyl benzoylacetate (56.8 g, 0.30 mol) and methyl vinyl ketone (20.8 g, 0.30 mol) in *tert*-butyl alcohol (75 ml) at 0°. The solution became brownish and then green. After 5 hr the re-action was worked up according to Walker to give a mixture of

General.-Melting points and boiling points are uncorrected. Spectroscopic data were determined on a Perkin-Elmer Infracord ir spectrophotometer, a Beckman DK uv spectrophotometer, a Perkin-Elmer Hitachi RMU-6 mass spectrometer, and a Varian A-60 or JEOLCO C-60H nmr spectrometer. The nmr spectra

⁽¹⁰⁾ R. Hoffmann, R. Bissell, and D. G. Farnum, J. Phys. Chem., 78, 1789 (1969).

⁽¹¹⁾ W. Borsche and W. Menz, Ber., 41, 209 (1908).
(12) N. L. Drake and J. R. Adams, J. Amer. Chem. Soc., 61, 1326 (1939).

⁽¹³⁾ G. Walker, ibid., 77, 3664 (1955).

crystalline material and oil. The mixture was triturated with ether and filtered to give 39.5 g of a crystalline compound, mp 122-125°, which, when recrystallized from methanol, had mp 125-127° (lit.¹³ 128-130°); ir (Nujol) 3400, 1707, 1693 cm⁻¹; nmr (CDCl₃) τ 2.7 (m, 10), 5.79 (br s, 1 H), 6.05 (q, 2 H), 7.4 (s, 2 H), 7.55 (m, 4 H), 9.02 (t, 3 H). The filtrate when evaporated yielded 29.7 g of a yellow brown oil, 9.

B. Decarboxylation of the Condensation Products.—The solid obtained from above (31.5 g) was treated with an 8% aqueous potassium hydroxide solution (250 ml) and refluxed for 12 hr. The mixture was then cooled and extracted with ether, which was then washed with water and dried over magnesium sulfate. Evaporation of the solvent resulted in 19.1 g of the product which was recrystallized from hexane-ether (80:20) to give 17.5 g of 3-phenylcyclohex-2-enone: mp 64.5-65.5° (lit.¹³ 63-66°); ir 1665 cm⁻¹; mmr (CDCl₃) τ 2.7 (m, 5 H), 3.64 (t, J = 1.5 cps, 1 H), 7.13-8.1 (complex m, 6 H). The brown oil (29.1 g) obtained in A was refluxed in 8% potassium hydroxide (250 ml) to give the desired ketone (7.5 g) as a brownish solid. This crude product when recrystallized from hexane-ether (80:20) gave 6.1 g of the pure ketone. The total yield of pure ketone was 23.6 g (46.5%).

1,3-Diphenyl-1,3-cyclohexadiene.—3-Phenylcyclohex-2-enone (6 g) in dry tetrahydrofuran was added to a Grignard reagent prepared from bromobenzene (18.3 g) and magnesium turnings (2.8 g) in dry ether (150 ml) under an argon atmosphere. The reaction was allowed to go on overnight and then worked up by addition of a concentrated solution of ammonium chloride. The organic layer, after drying over magnesium sulfate, was evaporated to give 5.7 g of a thick yellow oil which was taken up in 95% ethanol, and the solution was chilled to give white platelets, mp 89-93°. Recrystallization from 95% ethanol resulted in 4.9 g (66%) of the same type of crystals: mp 95-97° (lit.¹⁴ 98-99°); nmr (CDCl₃) τ 2.67 (m, 10 H), 3.33 (sextet, J = 1.5 cps, 1 H), 3.9 (dt, J = 1.5 cps, J = 4.5 cps, 1 H), 7.4 (m, 4 H).

hilf (CDC) 7 2.07 (nl, 10 17), 5.05 (GAACO, v = 1.5 Gpc, z = 7), 3.9 (dt, J = 1.5 cps, J = 4.5 cps, 1 H), 7.4 (m, 4 H). **Truxilloyl Chloride.**—This compound was prepared according to White.¹⁵ Treatment of α -truxillic acid (29.6 g, 0.1 mol) with thionyl chloride (300 ml) yielded crystalline acid chloride. Recrystallization from benzene-petroleum ether (60:40) gave white prisms (26.7 g, 81%): mp 121–123° (lit.¹⁵ 127–128°); ir (Nujol) 1785 cm⁻¹.

Di-tert-butyl Pertruxillate.—Truxilloyl chloride (22 g) was mixed with tert-butyl hydroperoxide (40 ml) in dry benzene, under a nitrogen atmosphere. The mixture was cooled in an ice-salt bath to 0°, and dry pyridine (25.0 ml) was added dropwise. The reaction mixture was allowed to stir for 12 hr. The contents of the flask were then washed with 5% hydrochloric acid in ice water to remove the excess of pyridine. The unreacted acid and traces of hydrochloric acid were removed by washing with potassium hydroxide solution (150 ml of a 5% solution). The organic layer was dried over magnesium sulfate and the solvent was evaporated under reduced pressure at room temperature. The solid residue (25.5 g) was recrystallized from ether-hexane (1:2) (150 ml). The resulting needles weighed 23.7 g (81.5%): mp 142-142.5°; ir 1750 cm⁻¹. Titration of the perester¹⁶ indicated that it was 95.7% active perester.

trans-1,3-Diphenylcyclobutane (5, X = H). A. By Pyrolysis of Di-tert-butyl Pertruxillate.-The perester (22.5 g) was suspended in p-cymene (600 ml of solvent, distilled at 207.5-208.5°), and the suspension was heated under a stream of nitrogen with stirring. The perester dissolved at around 55°. At 130° the solution turned yellowish and effervescence began which became vigorous at around 150°. After 1.5 hr the bubbling stopped, but heating was continued for 12 hr more. The reaction vessel containing a yellowish solution was then attached to a 36-in. Vigreux column and the bulk of the p-cymene was distilled (at 35° , 0.5 mm). The yellow pasty residue was taken in ethanol and chilled. The p-cymene dimer which crystallized was filtered off and the mother liquor was stripped of solvent and distilled through a 4-in. Vigreux column. p-Cymene was distilled first. The fraction which distilled at $125-140^{\circ}$ (1.0 mm) was rich in the desired product (70-80% as judged by nmr). The residue of distillation also contained 20-30% of the product. The abovementioned fraction and the residue were combined and redistilled to give 5.8 g of an oil $[110-123^{\circ} (0.25 \text{ mm})]$ containing ca. 90%

of the cyclobutane 5, (X = H) as judged by nmr. Column chromatography over silicic acid yielded 4.5 g (42%) of purer hydrocarbon as a thick oil. Recrystallization from methanol yielded needles: mp 40-41°; ir (film) 3030, 2980, 1610, 1500, 1450 cm⁻¹; nmr (CCl₄) τ 2.8 (m, 10 H), 6.4 (q, J = 7 cps, 2 H), 7.48 (t, J = 7 cps, 4 H).

Anal. Caled for $C_{16}H_{16}$: C, 92.26; H, 7.74; mol wt, 208. Found: C, 92.07; H, 7.60; mol wt, 208 (mass spectrum, parent peak).

B. By Reductive Deamination of Dimethiodide 5 [X = +N-(CH₃)₃].-Dimethiodide (14 g, 0.024 mol) (see below) was added to distilled liquid ammonia (400 ml) at -78° . Isopropyl alcohol (3.6 ml) was added and lithium ribbon (washed with petroleum ether to remove the oil) was cut and added in pieces until the blue color persisted for 2 min. The mixture was then allowed to stir at -78° for 30 min more and then ammonium chloride (10 g) was added. The ammonia was then allowed to evaporate, and the residue was taken in ether and washed with water and then hydrochloric acid solution. The ether solution was dried and evaporated to give a yellow fluorescent oil. The oil was distilled $[91^{\circ} (0.15 \text{ mm})]$ to give 3 g (60%) of a clear liquid. The nmr spectrum showed peaks characteristic of 1,3-diphenylcyclobutane plus some other peaks. However, 90-95% of the phenyl absorption was due to the diphenylcyclobutane based on the ratio of its methylene peak (τ 7.48) to the phenyl peak (τ 2.8). The mixture could not be separated by vpc, column chromatography, or fractional distillation but was successfully used in the preparation of dibromide 6.

1,3-Dibromo-1,3-diphenylcyclobutane (6).—1,3-Diphenylcyclobutane (2.2 g, 0.0105 mol) was dissolved in carbon tetrachloride (50 ml), and N-bromosuccinimide (4.3 g, 0.023 mol) and benzoyl peroxide (0.2 g) were added. The mixture was brought to reflux by means of an oil bath. When all of the N-bromosuccinimide was consumed, the succinimide was filtered and the solvent was removed at reduced pressure. The residue was taken up in ether. The ethereal solution yielded needles (800 mg): mp $145-145.5^{\circ}$ dec; nmr (CDCl₈) τ 2.6 (m, 10 H), 5.85 (s, 4 H).

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.46; H, 3.83; Br, 43.71. Found: C, 52.62; H, 3.94; Br, 43.65.

Addition of hexane to the ethereal mother liquor and cooling gave a solid (1.9 g) (total yield 69%) whose nmr spectrum showed peaks for the solid previously obtained and others at $\tau 2.7$ (10 H) and 6.0 (s, 4 H). Both isomers decompose when allowed to stay in air.

Anal. Caled for $C_{16}H_{14}Br_2$: C, 52.46; H, 3.83; Br, 43.71. Found: C, 52.62; H, 3.82; Br, 43.62.

1,3-Diphenyl-2,4-bis(dimethylamino)cyclobutane [5, X = N- $(CH_3)_2$].—The β -nitrostyrene photodimer (5, X = NO₂) (45 g, 0.15 mol) was placed in a 3-1. round-bottom flask, and zinc dust (300 g) and formaldehyde (250 ml of a 37% aqueous solution) were added. The suspension was warmed on a steam bath and formic acid (550 ml of a 88% aqueous solution) was added dropwise over a period of 4 hr with vigorous stirring. As soon as the reaction started, the external heat was discontinued since heat of reaction was sufficient to maintain the temperature at about 80-90°. Caution! In one run the formic acid accumulated without reacting and the reaction suddenly took off with explosive violence. After the addition was completed, the reaction was heated over a steam bath again for 6 hr more, and formic acid (two 200-ml portions) was added to ensure completion of the reaction. The insoluble material was then filtered and the filtrate was concentrated under reduced pressure at 60°. The concentrated solution was washed with benzene and the aqueous phase was made basic with sodium hydroxide solution. A white precipitate formed which was filtered, and the solid was washed with ether. The filtrate was also extracted with ether. The combined ethereal solution was washed with water and dried over magnesium sulfate. Evaporation of the ether yielded 38.5 g of a white solid which was recrystallized from ether-hexane (20:80) to give 35.5 g (79.9%) of pure **5** [X = N(CH₃)₂]: mp 125-127° (lit.¹⁵ 122-123°); ir (CHCl₃) 2990, 2950, 2850, 2800 cm⁻¹; mmr (CDCl₃) τ 2.75 (m, 10 H), 6.7 (A₂B₂ q, 4 H), 8.25 (s, 12 H).

1,3-Diphenyl-2,4-bis(dimethylamino)cyclobutane Dimethiodide [5, $X = {}^{+}N(CH_{\vartheta})_{\vartheta}$].--2,4-Diphenyl-1,3-bis(dimethylamino)cyclobutane (6.7 g) was dissolved in anhydrous acetone (50 ml) with a little warming. Methyl iodide (10 ml) was added and the mixture was warmed for 2 min. The flask was stoppered and allowed to stand for 0.5 hr. The dimethiodide was filtered and proved to be pure without any need for recrystallization, mp 222-225° (lit.¹⁵ 215-217°).

⁽¹⁴⁾ G. F. Woods and I. W. Tucker, J. Amer. Chem. Soc., 70, 2176 (1948).

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⁽¹⁶⁾ L. Silbert and D. Swern, Anal. Chem., 30, 385 (1958).

1,3-Diphenylcyclobut-2-enyl Cyanide (7, X = CN).--1,3-Dibromo-1,3-diphenylcyclobutane (6) (2 g, 5 mmol) was dissolved in acetonitrile (150 ml) and DMSO (60 ml) under a nitrogen atmosphere. Sodium cyanide (2 g) was added to the solution and the mixture was stirred at room temperature for 10 hr. The milky yellow solution was then poured into 1 l. of water and extracted with ether (two 300-ml portions). The ethereal solution was washed with water several times and then with saturated sodium chloride solution and was dried over magnesium sulfate. Evaporation of the solvent yielded a brownish oil which was chromatographed on Florisil. The desired product was eluted with hexane as a yellow oil (1.03 g, 82%): ir (neat) 2220 cm⁻¹; nmr (CCl₄) τ 2.70 (m, 10 H), 3.72 (s, 1 H), 6.79 (A₂B₂ q, J = 13cps, 2 H); mass spectrum m/e 231 (parent peak). The substance decomposed rapidly on standing at room temperature and was not analyzed.

1,3-Diphenylcyclobut-2-ene-1-carboxamide $(7, X = CONH_2)$. Sodium methoxide (commercial powder, 1.2 g, 22 mmol) was dissolved in DMSO (50 ml). Cyanide 7 (X = CN) (1.1 g, 4.7 mmol) in DMSO (5 ml) was added. The solution was stirred at room temperature under a nitrogen atmosphere. After 48 hr, the solution was poured into 800 ml of ice water and extracted with ether. The ether solution was washed with water several times and dried over magnesium sulfate. When the ether solution was concentrated to 15 ml and hexane was added, a white precipitate formed which was filtered and recrystallized from hereinitate formed which was intered and recrystanzed from hexane-ether to give 0.872 g (73%) of a white solid: mp 143– 145°; ir (CHCl₈) 3500, 3360, 1685 cm⁻¹; nmr (CDCl₈) τ 2.7 (m, 10 H), 3.31 (s, 1 H), 4.25 (br s, 2 H), 6.68 (A₂B₂ q, J = 13.1 cps, 2 H); mass spectrum m/e 249 (parent peak). The compound decomposed rapidly at room temperature and was not analyzed.

1-Methoxy-1,3-diphenylcyclobutene $(7, X = OCH_3)$.—Sodium iodide (3 g) was dissolved in DMSO (50 ml), and absolute methanol (1.5 ml) was added to the solution. Dibromide 6 (1.5 g of)the mixture of isomers) was dissolved in 5 ml of DMSO and added to the solution. After a while a yellow color developed which gradually turned red-brown (iodine). After 12 hr the solution was added to ice water (800 ml), and the cloudy solution was ex-tracted with ether. The ether solution was washed with a dilute sodium sulfite solution to remove the iodine and washed several times with water to remove the DMSO. The ether solution was dried and evaporated to give 0.953 g (98.5%) of an oil: ir $(CHCl_3)$ 1117 cm⁻¹; nmr (CCl₄) τ 2.75 (m, 10 H), 3.35 (s, 1 H), 6.82 (s, 3 H), 7.02 (A₂B₂ q, J = 13 cps, 2 H) (there were no other peaks evident in the nmr spectrum, and integration ratios were within 15% of the calculated values); mass spectrum m/e236. The compound was unstable at room temperature and was not analyzed.

Registry No.-1, 27617-85-2; 2, 27396-85-6; 3, 27396-86-7; 4, 27396-87-8; trans-5 (X = H), 25558-23-0; 5 [X = N(CH₃)₂], 19043-28-8; *cis*-6, 27396-24-3; trans-6, 27396-25-4; 7 (X = CN), 27396-88-9; 7 $(X = CONH_2)$, 27396-89-0; 7 (X = OMe), 27396-90-3; 1-phenylpentane-1,4-dione, 583-05-1; 3-phenylcyclopent-2-enone, 3810-26-2; 1,4-diphenyl-1,3-cyclopentadiene, 4982-34-7; 3-phenylcyclohex-2-enone, 10345-87-6; 1,3-diphenyl-1,3-cyclohexadiene, 10345-94-5; ditert-butyl pertruxillate, 27396-96-9.

Application of the Linnett Electronic Theory to Organic Chemistry. The S_N2 Transition State IV.

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Linnett structures for the SN2 transition state are proposed which differ from conventional dotted-bond structures $X \cdots CR_3 \cdots Y$ in that the three C-R bonds are weakened by L strain. Valence shell expansion is not required. Walden inversion is accounted for, and the energy price for retention is estimated at 11 kcal/mol for R = H and 16 kcal/mol for $R = CH_3$. The pattern of activation energies in alkyl halide exchanges is discussed in terms of secondary L strain, which also explains the rate accelerations brought about by conjugated unsaturation, α heteroatoms, and the α effect. The effect of L strain on entering and leaving groups is also assessed. The discussion includes proton transfer and displacements on heteroatoms. Hydrogen bonds and trihalide ions are presented as examples of reactions with negative activation energy, or "frozen transition states," existing when L strain is exceptionally low. Deviations from simple kinetic-thermodynamic relationships, such as the Brønsted equation, are stressed. The E2C mechanism is critically discussed.

One of the most common devices in chemistry is the transition state picture in which dotted bonds are used to represent normal ones that are in a state of either formation or dissolution. The dots are meant to express our ignorance of the structures of transition states as compared to stable molecules but are frequently taken to mean much more than that, in particular a state intermediate in properties between reactant and product. However, in opposition to this simple picture, for many reactions, is the disparity between the kinetic and thermodynamic products and, most significantly, the need for activation energy.

It is possible, by means of the Linnett electronic theory,^{1,2} to replace many dotted-bond structures with better defined, yet simple, ones with unique properties that are not derived immediately from reactants or products. One such property is L strain,^{3,4} a type of

 J. W. Linnett, J. Amer. Chem. Soc., 83, 2643 (1961).
 J. W. Linnett, "The Electronic Structure of Molecules," Methuen and Co. Ltd., London, 1964.

angle strain not yet recognized in conventional molecular representations, but clearly derived form Linnett's double-quartet theory. L strain must nevertheless be latent in conventional theory also, since the Linnett theory is based upon the same underlying quantum mechanical postulates. In contrast with an ordinary bent bond, an L-strained bond suffers from lack of coincidence of the two spin sets about one or more atoms, which weakens the bond in the same way that bending does, namely by forcing the bonding electrons away from their optimum positions. L-Strained bonds are not bent, however. This topic is fully discussed in papers I and II of this series. The policy will be continued here of limiting the discussion to first row elements for the most part.

A prominent example of a dotted-bond transition state is that for the SN2 reaction, depicted universally

⁽³⁾ R. A. Firestone, Tetrahedron Lett., 971 (1968).

⁽⁴⁾ R. A. Firestone, J. Org. Chem., 34, 2621 (1969).