hydrogens instead of six. The infrared spectrum gave an OH band at 3360, C–D bands at 2235, 2150, and 2060, and a noticeable carbonyl band at 1645 cm.<sup>-1</sup>. The purity was sufficiently good for our n.m.r. studies. Further attempts to remove the last traces of ketone by treatment with hydroxylamine in ethanolic OH solution resulted in degration of the alcohol.

Tricyclopropylcarbinol. Lithium sand was prepared by melting 4 g. of lithium in hot Nujol and shaking vigorously. As soon as the sand had formed, the Nujol was cooled rapidly and the sand was separated by diluting the Nujol with ether and filtering through a glass plug. The sand was ether washed and then suspended in 200 ml. of dry ether in a three-neck, roundbottom flask under N<sub>2</sub> atmosphere. Cyclopropyl bromide (Aldrich), 25 g., was added dropwise at 0° with vigorous stirring. After the addition was completed another hour was allowed for completion of the reaction at 0°. Then 16.5 g. of dicyclopropyl ketone was added dropwise followed by an additional 3 hr. of reaction at 0° and 28 hr. at room temperature. Hydrolysis was completed with an excess of distilled water and the ether layer was separated, washed, and dried over anhydrous MgSO<sub>4</sub>. The ether was aspirated and (14.1 g. of) the title alcohol was obtained on vacuum distillation through a jacketed, 8-in. Vigreux column with a boiling range of 87 to 88.5° (10 mm.) (lit.<sup>25</sup> b.p. 88.5° at 10 mm.).

Preparation of Tricyclopropylcarbonium Tetrafluoroborate. Twelve grams of tricyclopropylcarbinol was dissolved into 300 ml. of propionic anhydride. The solution was then cooled to between 15 and 20° while a 1.1 mole excess of 50% aqueous HBF<sub>4</sub> was added in small aliquots. Crystallization occurs, and the BF<sub>4</sub><sup>-</sup> salt was obtained in 21% yield.

(25) H. Hart and P. A. Law, J. Am. Chem. Soc., 81, 320 (1959).

# Approaches to "Push-Pull" Stabilized Cyclobutadienes<sup>1</sup>

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It is predicted that cyclobutadienes substituted by conjugated electron-donor and electron-acceptor groups will be stabilized. In approaches to such systems several nitrodimethylaminocyclobutenes have been prepared. However, dehydrohalogenations under mild conditions which should generate the nitrodimethylaminocyclobutadienes lead chiefly to tarry products. Dehydrobromination to produce a tetrasubstituted cyclobutadiene with its dimethylamino group conjugated with both nitro and benzoyl groups similarly leads chiefly to tarry products. Studies on a push-pull substituted cyclobutenone show that enolization to the cyclobutadiene is slow compared with hydrolysis of the compound. A number of cyclobutene rearrangements have been encountered, including an unusual ring-chain tautomeric equilibrium.

### Introduction

Overwhelming evidence is available that the cyclobutadiene system is kinetically and thermodynamically unstable.<sup>2a</sup> This is reflected in the properties not only of the parent substance, but also of a variety of derivatives. Thus even tetraphenylcyclobutadiene, an extensively conjugated and rather hindered compound, dimerizes on generation.<sup>2b</sup> Theoretical explanations for such instability are available.<sup>3</sup> However, some stable cyclobutadiene derivatives have been prepared. One class of such derivatives, complexes of cyclobutadienes with transition metals, is of considerable interest, but bears little electronic resemblance to cyclobutadiene itself.<sup>4</sup> Another sort of derivative is exemplified by biphenylene (A) and the recently prepared<sup>5</sup> naphthalene derivative (B). In



these cases the system is stable because the structures drawn are not the sole, or even the principal, resonance forms. In other resonance forms it becomes apparent that A and B may also be considered to be derivatives of the rather stable<sup>6</sup> dimethylenecyclobutane system.

The same principle, that a compound may be stable if a cyclobutadiene structure is only one of the important resonance forms, is the valence-bond explanation of the postulated<sup>7</sup> "push-pull" effect. Simple molecular orbital calculations<sup>7</sup> show that cyclobutadienes substituted with conjugated electron-donor and electron-acceptor groups should have considerable resonance energy. Furthermore, the degeneracy of

<sup>(1)</sup> Taken in part from the Ph.D. Thesis of D. Kivelevich, Columbia University, 1961. Support of this work by the National Science Foundation and the Sloan Foundation is gratefully acknowledged.

<sup>(2) (</sup>a) For a review of some of the evidence, cf. A. Streitwieser, Jr.,
"Molecular Orbital Theory," John Wiley and Sons, Inc., New York,
N. Y., 1961, p. 261; (b) H. H. Freedman, J. Am. Chem. Soc., 83, 2195 (1961); R. C. Cookson and D. W. Jones, J. Chem. Soc., 1881 (1965).

<sup>(3)</sup> E. g., M. J. S. Dewar and G. J. Gleicher, J. Am. Chem. Soc., 87, 685 (1965), and many earlier calculations.

<sup>(4)</sup> H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc., 1969 (1956); R. Criegee and G. Schröder, Ann., 623, 1 (1959); H. H. Freedman, J. Am. Chem. Soc., 83, 2194 (1961); P. M. Maitlis and M. L. Games, *ibid.*, 85, 1887 (1963).

<sup>(5)</sup> M. P. Cava, B. Hwang, and J. P. van Meter, *ibid.*, 85, 4032 (1963).
(6) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, 74, 4579 (1952).

<sup>(7)</sup> S. L. Manatt and J. D. Roberts, J. Org. Chem., 24, 1336 (1959), and our own calculations.

 $\psi_2$  and  $\psi_3$  in cyclobutadiene itself<sup>8</sup> is strongly split in such substituted cases. This is as expected since the systems should have an appreciable contribution of a noncyclobutadiene resonance form. The exact mag-



nitude of the effects depends of course on the natures of X and Y, but the stability of such derivatives is expected to increase as structure D becomes more important. Accordingly, we have investigated a system in which the "push-pull" effect should be maximized, letting X be a dialkylamino group and Y a nitro group.

#### **Results and Discussion**

Roberts has reported<sup>9</sup> a number of SN2' displacements on cyclobutenyl halides. We find that reaction of 1-phenyl-3,3-difluoro-4,4-dichlorocyclobutene (I)<sup>10</sup> with sodium nitrite<sup>11</sup> affords the nitrocyclobutene II in over 50% yield. The structure follows from the analytical and spectral data and subsequent transformations. It was hoped that II might react directly with an amine to afford a cyclobutadiene derivative, by a sequence related to that (*vide infra*) by which a nitroaminocyclobutene (VI) was formed. However, the products with a variety of secondary amines were open-chain butadienes (III). The structures follow from analytical and spectral data, including a large  $J_{\rm H-F}$  in the n.m.r. which shows that the vinyl proton is vicinal to the fluorine.



Apparently II reacts with amines by SN2' substitution, rather than by elimination of HF as in the V  $\rightarrow$  VI conversion. In an attempt to force HF elimination, II was treated with butyllithium. An impure lithium salt (IV) was formed which did not lose fluoride under ordinary conditions and regenerated II (or deuterio II) on treatment with water (or D<sub>2</sub>O). On heating in

(11) For this method of synthesis of nitro compounds, cf. N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *ibid.*, 78, 1497 (1956).

amines the salt IV was destroyed with the formation of tarry materials.



Hydrogenation converted II directly to the dechlorinated cyclobutane V. Apparently the second mole of hydrogen is absorbed more rapidly than the first, since stopping the reduction halfway produced only a mix-



ture of II and V. The cyclobutene II did not react with diimide.<sup>12</sup> Treatment of V with dimethylamine afforded the nitroenamine VI in good yield. The structure is established by the usual analytical and spectral data, including cyclobutene absorption at  $6.02 \ \mu^{13}$  and the expected n.m.r. spectrum. The Nmethyl groups are seen as two separate peaks<sup>14</sup> at  $\delta$ 3.6 and 2.8; both the resolution into two peaks and the chemical shifts (dimethylformamide has  $\delta$  2.88 and 2.97 while dimethylaminoethanol has a single Nmethyl peak at  $\delta$  2.25) indicate strong conjugation in the nitroenamine system. For chemical structure proof VI was hydrolyzed to 4-nitro-3-phenylbutyramide (VII), and this in turn to phenylsuccinic acid, identical with an authentic sample.<sup>15</sup> Treatment of V with



$$HO_2C - \dot{C}H - CH_2 - CO_2H$$

(12) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, 83, 3725 (1961).

(13) As expected, the cyclobutenes showed a C = C stretch at lower wave lengths than the open-chain analogs, e.g., III and XV.

(14) Two separate NCH<sub>3</sub> peaks were shown at room temperature by VI, X, XIII, XVIII, XVIII (in CH<sub>2</sub>Cl<sub>2</sub> or pyridine), and XVI and XV (at  $-20^{\circ}$ ). A single NCH<sub>3</sub> peak was shown by VIII, XII, and XVII (in CCl<sub>4</sub>), and XIV and XV (at  $+70^{\circ}$ ). In some cases broadening of these peaks was apparent, indicating that the spectra were close to the transition point. The factors which determine whether or not rotation of the dimethylamino group produces a single NCH<sub>4</sub> signal in the n.m.r. include: (1) the rate of rotation, which is influenced by the strength of the conjugative interaction and also by steric factors, particularly steric destabilization of the two methyls in the coplanar conformation, which determines what rate of rotation will be required to produce n.m.r. averaging. The experimental observations can be explained *post factor* in these terms.

(15) Purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis.

<sup>(8)</sup> The relation of this degeneracy to the stabilities of such species is not clear. On the basis of our unpublished work on unsymmetrically substituted cyclopentadienyl cations, it seems certain that cyclobutadienes of the type proposed here would have singlet ground states.

<sup>(9)</sup> M. C. Caserio, H. E. Simmons, Jr., A. E. Johnson, and J. D. Roberts, J. Am. Chem. Soc., 82, 3102 (1960).

<sup>(10)</sup> J. D. Roberts, G. B. Kline, and H. E. Simmons, Jr., *ibid.*, 75, 4765 (1953).

pyrrolidine produced the pyrrolidine enamine analogous to VI.

The hydrogens on C-4 of the nitroenamine are activated by conjugation with the nitro group, and they can be readily replaced by base-catalyzed halogenation. With bromine and pyridine, VI was converted to a 4,4-dibromo derivative (VIII); this could be hydrolyzed to phenylbromomaleic anhydride (IX).<sup>16</sup> With I<sub>2</sub> and



pyridine VI affords a 4-monoiodo derivative (X), even with excess  $I_2$ .



Numerous dehydrohalogenations of both VIII and X afforded only brown, tarry materials which defied all attempts at characterization. Thus VIII with triethylamine yielded triethylamine hydrobromide, but careful chromatography produced only recovered VIII and brown tars. Ultraviolet spectra of reaction mixtures showed no significant peaks in addition to those from residual starting material. Furthermore, treatment of VIII with 1 equiv. of potassium t-butoxide at room temperature for 30 min. resulted in complete base consumption, but 20% of VIII was recovered and the other products were tars. Similar results were obtained with sodamide, aqueous sodium hydroxide, and silver oxide. Runs in the presence of furan, in an attempt to trap<sup>17</sup> an intermediate cyclobutadiene, also failed to produce characterizable products. Treatment of the iodo compound X with 1 equiv. of potassium t-butoxide for 2 min. at room temperature produced 40% of recovered starting materials and 60% of iodide ion, but in addition to X the organic products were brown-toblack tars with ill-defined spectra, unresolved by careful chromatography.

Although the formation of ill-defined tars in these reactions is certainly ambiguous evidence about the stabilities of the desired cyclobutadienes, it was decided to try for an even more stabilized case. The predicted resonance stabilization of a nitroamino-cyclobutadiene is essentially associated with the localized nitroenamine system, involving only one of the double bonds. It was felt that greater stability might be found if the amino group were conjugated with *two* electron-withdrawing groups. Both for this reason and because of expected steric effects, structure E was selected.



Direct benzoylation of the cyclobutene VI to produce XIII failed, but reaction with benzaldehyde and base yielded the  $\alpha$ -hydroxybenzyl derivative XI. *p*-Nitrobenzaldehyde also afforded the related adduct. The alcohol XI could be dehydrated to XII, the benzylidene-cyclobutene. This reacts with N-bromosuccinimide to give a simple adduct of NBS across the exocyclic double bond; it is interesting that the expected benzylic bromination of XII would involve a radical with a cyclobutadiene resonance form. Oxidation of XI with pyridine and chromic oxide yields the benzoyl com-



pound XIII, and this on bromination affords XIV.



The properties of XIV are very unusual. Thus by careful low-temperature crystallization, it is possible to prepare the yellow XIV free of a persistent red impurity. Then it shows the usual nitroenamine ultraviolet absorption near 380 m $\mu$ , and the infrared stretch at 6.02  $\mu$ , as well as the other expected spectroscopic properties. However, on standing or heating, the solutions show changed spectra and they deposit both yellow XIV and the red material again. By selective crystallization, it was possible to purify the red substance and identify it by analytical and spectral properties as the butadiene XV, a valence tautomer of XIV. The two have identical analyses but grossly different infrared, ultraviolet, and n.m.r. spectra; in particular, both XIV and XV have two different N-methyl peaks14 in the n.m.r. at  $-20^{\circ}$  which coalesce into a single peak for each compound at  $+70^{\circ}$ , but those in the nitroenamine XIV are at lower field than those of the less polarized benzoylenamine XV. N.m.r. studies show a ratio XIV/XV of about 3 at room temperature and about 9 at  $-20^{\circ}$ ; as expected, the proportion of open chain isomer XV is increased at the higher temperature.

<sup>(16)</sup> The structure is established by analytical and spectral data and the virtual identity of the infrared spectrum with that of phenylchloromaleic anhydride

<sup>(17)</sup> Cf. M. P. Cava and M. J. Mitchell, J. Am. Chem. Soc., 81, 5409 (1959).



The usual position<sup>18</sup> of a cyclobutene-butadiene equilibrium is reversed in this case because nitroenamine conjugation is more favorable than that in a benzoylenamine. The effect of the bromine in establishing an equilibrium in XIV which was not observed in XIII (or in any other of our nitroenamines) is presumable to furnish steric crowding in XIV. All spectroscopic studies showed that equilibration was complete in a few hours; by observation of changes in the ultraviolet spectra of pure XIV and XV in ethanol at 27°, we found  $k_{\text{XIV}} \rightarrow \text{XV} = 3.5 \times 10^{-3} \text{ min.}^{-1} \text{ and } k_{\text{XV}} \rightarrow \text{XIV} = 11.2 \times 10^{-3} \text{ min.}^{-1}$ . The ratio of these rate constants gives an equilibrium constant of 0.31, in agreement with the equilibrium constant from n.m.r. studies.

The equilibrium mixture of XIV and XV was treated at room temperature with triethylamine. In a run lasting for 5 days about 1 equiv. of triethylamine hydrobromide was formed, but the only organic product in addition to brown tars was a few per cent of XIII from apparent reduction. Over shorter times the XIV-XV mixture could also be recovered, with XIII and brown tars. Runs in the presence of furan also produced only tarry products. It seems likely that the cyclobutadiene E is formed, but that it is unstable under even these mild conditions.

In view of this evidence on the difficulty of isolating the desired "stabilized" cyclobutadienes, it was decided to try detecting them as transient intermediates. Thus the ketone XVII was selected as a synthetic goal; deuterium exchange could be used to demonstrate transient enol or enolate formation, and the ease of this process compared with suitable models. Although cyclobutenones cleave readily and apparently do not enolize,19 we hoped that enolization to form a "stabilized" cyclobutadiene might be more favorable. Hydrolysis involving ring-chain tautomerism<sup>20</sup> should also be suppressed by the nitroenamine conjugation effect.

The successful synthesis of XVII proceeded from X by formation of a nitrate ester, and basic elimination of nitrite.<sup>21</sup> The ketone XVII proved to be rather sensi-



(18) Cf. R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publications, Inc., New York, N. Y., 1963, Chapter 4. (19) See, for instance, J. D. Roberts, G. B. Kline, and H. E. Simmons,
Jr., J. Am. Chem. Soc., 75, 4765 (1953).
(20) F. F. Silversmith, Y. Kitahara, M. C. Caserio, and J. D. Roberts,

ibid., 80, 5840 (1958).

tive to base, and only hindered 2,6-lutidine proved suitable for the elimination step. Shaking a solution of XVII in carbon disulfide with D<sub>2</sub>O produced no change in its n.m.r. spectrum over several days; more significantly, the n.m.r. spectrum of XVII in pyridine with D<sub>2</sub>O changed over a few hours, but the rate of disappearance of the N-methyl signals (in favor of a new band at higher field) was the same as the rate of disappearance of the benzylic proton in XVII in favor of a new peak at lower field. Apparently exchange of the proton in XVII is slow compared with hydrolysis of the compound.

In principle, even more stabilization might be found with an electron donor stronger than amino. For instance, the enolate of a nitrocyclobutenone should have a major contribution of structure F, and physical studies might be used to determine its actual electronic configuration. In an approach to such a system we



treated 2,2-dichloro-3-phenylcyclobutenone (XVIII)<sup>10</sup> with sodium nitrite, as in the synthesis of II, and obtained a compound, m.p. 156-157° dec., which analyzes for G, the nitrocyclobutenone. However, the infrared spectrum shows a hydroxyl band at 2.83  $\mu$ , carbonyl absorption at 5.60  $\mu$ , and no bands in the normal nitro region. The n.m.r. spectrum shows five phenyl protons at  $\delta$  7.7 and one proton at 11.1, and the ultraviolet has  $\lambda_{\text{max}}$  301 m $\mu$  ( $\epsilon$  18,300). These data are consistent with structure H, the aci-nitro compound, but structure J is not completely excluded. On heating or treatment with base, this compound is converted to N-hydroxyphenylchloromaleimide (XIX), synthesized unambiguously from the corresponding maleic anhydride. The hydroxylic proton in H (or J)



exchanges rapidly with  $D_2O$ , of course, but all attempts to prepare an anion lead to rearrangement to XIX. Since all attempts at chemical characterization also lead to derivatives of phenylchloromaleic anhydride it must be concluded that the nitrocyclobutenone system is unstable, rearranging too readily to permit studies on the anion.

(21) Cf. M. P. Cava, D. R. Napier, and R. J. Pohl, ibid., 85, 2076 (1963).

## **Experimental Section**

1-Phenyl-2-chloro-3,3-difluoro-4-nitrocyclobutene (II). 1-Phenyl-3,3-difluoro-4,4-dichlorocyclobutene (I) was prepared by the reported procedure<sup>10</sup> in 79% yield. A stirred solution of 117.5 g. (0.50 mole) of I, 65 g. of urea, and 120 g. of catechol in 500 ml. of dry dimethylformamide was treated with 36.8 g. (0.53 mole) of sodium nitrite, added over 4 hr. in *ca.* 20 equal portions.<sup>11</sup> The mixture was then stirred at room temperature for 6 hr. and poured into 2 l. of ice-water. Extracting with four 200-ml. portions of 1:3 etherpetroleum ether (b.p. 30-60°), washing the combined extracts with 5% NaHCO<sub>3</sub>, drying, and solvent removal gave crude nitro compound (104 g., 85%). This was recrystallized from methanol, yielding 66 g. (54%) of pure II, m.p. 64-65°.

Anal. Calcd. for  $C_{10}H_6ClF_2NO_2$ : C, 48.90; H, 2.46; Cl, 14.44; F, 15.47; N, 5.70. Found: C, 48.57; H, 2.11; Cl, 14.20; F, 15.21; N, 5.80.

In the ultraviolet, the compound had  $\lambda_{max} 262 \text{ m}\mu$ ( $\epsilon 21,400$ ). The infrared spectrum had  $\lambda\lambda_{max} 6.4$  and 7.4  $\mu$  (NO<sub>2</sub>) and the other expected bands, including one at 6.17  $\mu$  (C==C). In the n.m.r. there was a fiveproton aromatic sharp peak at  $\delta 2.5$  and a one-proton double doublet ( $J_1 = 2.2$  c.p.s.,  $J_2 = 0.9$  c.p.s. for couplings to adjacent F's) at  $\delta 5,9$ .

Reaction of II with Amines. Addition of 0.50 g. of II to 5 ml. of dry diethylamine at room temperature produced an immediate yellow precipitation. After 24 hr. the precipitate was collected and recrystallized from benzene-petroleum ether to give 0.32 g. (52%) of *1-diethylamino-1-phenyl-2-chloro-3-fluoro-4-nitrobutadiene* (III), m.p. 182–183°.

Anal. Calcd. for  $C_{14}H_{16}ClFN_2O_2$ : C, 56.28; H, 5.40; Cl, 11.87; F, 6.36; N, 9.38. Found: C, 56.22; H, 5.20; Cl, 11.82; F, 6.56; N, 9.60.

In the ultraviolet the compound had  $\lambda\lambda_{max} 276 \text{ m}\mu$ ( $\epsilon 10,900$ ) and 377 m $\mu$  ( $\epsilon 11,400$ ). The infrared spectrum showed bands at 6.60 and 7.70  $\mu$  (NO<sub>2</sub>) and the n.m.r. showed a five-proton band at  $\delta$  7.3 (aromatic), a one-proton doublet (J = 23 c.p.s.) at 5.2 (vinyl H, coupled to vicinal F), the four-proton quartet at 3.2, and six-proton triplet at 1.4 of the ethyl groups. The compound was insoluble (and unchanged) in 12 N HCl.

In a similar fashion the *1-di-n-propylamino-1-phenyl-2-chloro-3-fluoro-4-nitrobutadiene* (IIIb) was prepared, m.p.  $115.5-117^{\circ}$ , in 72% yield.

Anal. Calcd. for  $C_{16}H_{20}ClFN_2O_2$ : C, 58.80; H, 6.17; Cl, 10.85; F, 5.81; N, 8.57. Found: C, 58.62; H, 6.54; Cl, 10.55; F, 5.55; N, 8.82.

The ultraviolet spectrum showed  $\lambda\lambda_{max}$  277 m $\mu$  ( $\epsilon$  11,400) and 377 m $\mu$  ( $\epsilon$  11,900).

The di-*n*-butylamino derivative (IIIc), m.p.  $123-124^{\circ}$ , was prepared in 76% yield and showed  $\lambda\lambda_{max}$  278 m $\mu$ ( $\epsilon$  11,700) and 378 m $\mu$  ( $\epsilon$  12,100) and correct analytical values. The dimethylamino derivative (IIId), m.p. 173-175°, had spectra similar to these and also gave correct analytical values.

Reaction of II with Butyllithium. A solution of II (1.265 g., 5.1 mmoles) in 30 ml. of hexane was added to a stirred, cooled solution of butyllithium (11.5 mmoles) in 30 ml. of hexane. After 1 hr. the precipitate was collected; on standing, a second crop was deposited (1.096 g. total). Vacuum drying and analysis

indicated that this was the rather impure lithium salt (IV).

Anal. Calcd. for  $C_{10}H_5ClF_2LiNO_2$ : C, 47.74; H, 2.00. Found: C, 46.14; H, 4.13.

The compound was insoluble in ether and in hydrocarbons. In a separate run 200 mg. of II yielded 186 mg. of washed, dried salt, which was suspended in ether and treated with aqueous NH<sub>4</sub>Cl. The ether layer yielded 95 mg. of II, and acidic work-up of the original hexane filtrate afforded an additional 72 mg. of II (total recovery 83%). In another run the salt from 200 mg. of II was added to 5 ml. of ether and 5 ml. of D<sub>2</sub>O. The ether layer was dried and concentrated and the residue, after charcoal treatment, afforded 13 mg. of deuterated II, m.p. 61.5-62°. In the infrared it showed bands at 3.41 and 4.42  $\mu$ , vs. the bands for II at 3.31 and 3.41  $\mu$ .

1,1-Difluoro-2-nitro-3-phenylcyclobutane (V). A solution of II (10.0 g., 0.040 mole) in 150 ml. of methanol was hydrogenated in the presence of 10.5 g. of CaCO<sub>3</sub> with 1.3 g. of 5% Pd-C. The hydrogenation was stopped after uptake of 2.1 l. (0.085 mole at 26°, 765 mm.) and the solids were filtered off. The solvent was removed, the residual oil was taken up in ether and washed with water, and the ether layer was dried and concentrated, leaving crude V as a light yellow oil (7.5 g., 87% crude yield). Distillation afforded pure V, b.p. 110-120° (0.8 mm.) as a clear, colorless oil (6.1 g., 70%). The analytical sample was redistilled.

Anal. Calcd. for  $C_{10}H_{9}F_{2}NO_{2}$ : C, 56.31; H, 4.25; F, 17.81; N, 6.56. Found: C, 56.23; H, 4.32; F, 14.65; N, 6.94.

If the hydrogenation was not interrupted, 2 more moles were taken up and an 80% yield of crude 2,2-difluoro-4-phenylbutyraldoxime could be isolated, m.p.  $89-97^{\circ}$ . Several recrystallizations from ethanol gave colorless platelets, m.p.  $96-99^{\circ}$ .

Anal. Calcd. for  $C_{10}H_{11}NOF_2$ : C, 60.29; H, 5.57; F, 19.08; N, 7.03. Found: C, 60.10; H, 5.54; F, 19.13; N, 7.31.

The infrared spectrum (KBr) showed an intense peak at 3.08 and a band at 6.25  $\mu$ . Treatment of II with 100% excess of potassium azodicarboxylate and acetic acid<sup>12</sup> led to recovery of starting material (92%).

*I-Dimethylamino-2-nitro-3-phenylcyclobutene (VI).* A solution of 5.802 g. of V in 25 ml. of chloroform was added over 45 min. to a cooled  $(0-5^{\circ})$  solution of 5.0 g. of dimethylamine in chloroform. The mixture was stirred in the cold for 45 min. further, then washed with water, dried, and concentrated. The solid residue was recrystallized from methanol, affording 4.50 g. (76%) of pure *I-dimethylamino-2-nitro-3-phenylcyclobutene (VI)* as yellow needles, m.p. 125–126°.

Anal. Calcd. for  $C_{12}H_{14}N_2O_2$ : C, 66.03; H, 6.46; N, 12.84. Found: C, 66.33; H, 6.59; N, 13.02.

The ultraviolet spectrum had  $\lambda_{\text{max}}$  379 m $\mu$  (log  $\epsilon$  4.32) and the infrared spectrum had bands at 6.02 (C=C)<sup>13</sup> and 7.2  $\mu$ . In the n.m.r. there was a fiveproton aromatic band at  $\delta$  7.2, two<sup>14</sup> three-proton singlets at 3.6 and 2.8 (NCH<sub>3</sub> groups), a one-proton doubled doublet (J = 6 and 2 c.p.s.) at 4.1, another (J = 13and 6 c.p.s.) at 2.7, and a third (J = 13 and 2 c.p.s.) at 2.0.

A suspension of 100 mg. of VI in 5 ml. of 20% H<sub>2</sub>SO<sub>4</sub> was heated at 80° for 30 min. On cooling, 43

mg. (48%) of  $\alpha$ -phenylsuccinic acid deposited, m.p. 164–165°, identical with an authentic sample.<sup>15</sup>

A suspension of 1.0 g. of VI in 40 ml. of 75% aqueous acetic acid with 10 g. of potassium acetate was stirred at 40–50° until the yellow color faded (*ca.* 20 min.). Normal aqueous work-up afforded 860 mg. (78%) of 4-nitro-3-phenyldimethylbutyramide (VII), m.p. 91–93°, raised to 93–94° on recrystallization from ether.

Anal. Calcd. for  $C_{12}H_{16}N_2O_3$ : C, 60.99; H, 6.83; N, 11.86. Found: C, 61.38; H, 6.91; N, 11.71.

In the infrared there were bands at 6.2 (amide C=O) and at 6.5 and 7.25  $\mu$  (NO<sub>2</sub>). Hydrolysis with 20% H<sub>2</sub>SO<sub>4</sub> (*vide supra*) afforded  $\alpha$ -phenylsuccinic acid in 69% yield.

On a preparative scale, it proved possible to synthesize VI in 50% over-all pure yield directly from the crude hydrogenation product V without distillation.

Treatment of V with pyrrolidine (as described above with dimethylamine) afforded a 73% yield of *l-pyr-rolidino-2-nitro-3-phenylcyclobutene*, m.p. 128–129°.

Anal. Calcd. for  $C_{14}H_{16}N_2O_2$ : C, 68.83; H, 6.13; N, 11.46. Found: C, 68.55; H, 6.63; N, 11.42.

1-Dimethylamino-2-nitro-3-phenyl-4,4-dibromocyclobutene (VIII). A solution of  $Br_2$  (9.2 mmoles) in CCl<sub>4</sub> was added dropwise to 1.0 g. (4.6 mmoles) of VI and 1.8 g. (23 mmoles) of pyridine in 100 ml. of chloroform at 0-5° with stirring. After washing, drying, and concentrating, the residual oil was crystallized from methanol to yield 745 mg. (42%) of pure dibromo compound VIII, m.p. 134-135° dec.

Anal. Calcd. for  $C_{12}H_{12}Br_2N_2O_2$ : C, 38.32; H, 3.22; Br, 42.50; N, 7.45. Found: C, 38.15; H, 3.83; Br, 41.94; N, 7.60.

The ultraviolet spectrum had  $\lambda_{max}$  379 m $\mu$  (log  $\epsilon$  4.22) and the infrared spectrum had bands at 6.1 (C=C) and 6.38 and 7.18  $\mu$  (NO<sub>2</sub>). In the n.m.r. VIII showed five phenyl protons at  $\delta$  7.3, a one-proton singlet at 5.0, and a six-proton singlet <sup>14</sup> at 3.5.

A suspension of VIII (98 mg.) was hydrolyzed for 45 min. in refluxing 20% H<sub>2</sub>SO<sub>4</sub> to yield 25 mg. of sublimed *1-bromo-2-phenylmaleic anhydride* (IX), m.p. 60–64° (sublimes).

Anal. Calcd. for  $C_{10}H_5BrO_3$ : C, 47.46; H, 1.99; Br, 31.58. Found: C, 47.71; H, 2.17; Br, 31.53.

The infrared spectrum had bands at 5.44, 5.48, and 5.66  $\mu$  (anhydride) and the entire infrared (and ultraviolet) spectrum was very similar to that of 1-chloro-2-phenylmaleic anhydride.<sup>22</sup>

*I-Dimethylamino-2-nitro-3-phenyl-4-iodocyclobutene* (X). A solution of 3.45 g. (13.6 mmoles) of  $I_2$  in 80 ml. of chloroform was added over 1 hr. to a solution of 1.75 g. (8.0 mmoles) of VI and 3.22 g. (41 mmoles) of pyridine in 80 ml. of chloroform at room temperature. The precipitated pyridine-hydrogen diiodide was removed, and the solution was washed with aqueous NaHSO<sub>3</sub>, then water, and dried. Solvent removal and methanol trituration yielded the iodo compound X, 2.14 g. (77%), m.p. 150° dec. Recrystallization from methanol yielded 1.73 g. (63%), m.p. 150.5–152° dec.

Anal. Calcd. for  $C_{12}H_{13}IN_2O_2$ : C, 41.88; H, 3.80; I, 36.87; N, 8.14. Found: C, 41.80; H, 3.85; I, 37.04; N, 8.23.

(22) G. E. Ecke, L. R. Buzbee, and A. J. Kolka, J. Am. Chem. Soc., 78, 79 (1956).

The infrared spectrum had peaks at 6.02, 6.72, 6.90, 7.24, 7.70, 8.20, and 10.76  $\mu$ . The ultraviolet spectrum showed  $\lambda_{max}$  384 m $\mu$  (log  $\epsilon$  4.27). The n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub> solvent taken with  $\delta$ CH<sub>2</sub>Cl<sub>2</sub> = 5.33 p.p.m.) showed five phenyl protons at  $\delta$  7.32, one-proton (apparent) singlets at 4.44 and 4.22, and two<sup>14</sup> threeproton broad peaks at 3.64 and 3.14. A check in CHCl<sub>3</sub> showed that no peaks had been hidden.

Dehydrohalogenations of VIII and X. Numerous reactions of VIII with triethylamine yielded recovered VIII plus dark, tarry products. Thus 564 mg. of VIII and 3.04 g. of purified triethylamine in 30 ml. of chloroform were allowed to stand for 24 hr., then refluxed for 40 hr. During this time the mixture became dark brown, but no significant peaks appeared in the ultraviolet spectrum in addition to those of VIII. The solution was evaporated *in vacuo* and the black residue was extracted with ether, affording 180 mg. of brown oil. With methanol this deposited 40 mg. of VIII; only dark brown tars could be isolated from the mother liquors.

A similar mixture with an excess of furan was kept at room temperature for 9 days. Although a 35%yield of triethylamine-HBr was isolated, m.p. 244-247°, no other defined products could be isolated and 40% of VIII was recovered. Similar results were obtained when furan was omitted.

When VIII (59 mg., 0.157 mmole) was added to 2 ml. of potassium *t*-butoxide (0.17 mmole by titration) in *t*-butyl alcohol, the solution darkened rapidly. After 30 min. at room temperature aqueous ether processing yielded a neutral (phenolphthalein) aqueous layer. The ether layer afforded recovered VIII, 13 mg., m.p.  $129-130^{\circ}$ , and brown residues.

Treatment of VIII with sodamide in ammonia for 15 min. afforded recovered VIII plus tars, as did reaction with 0.05 N NaOH in 50% aqueous dioxane for 78 hr. at room temperature. In the latter case 2 equiv. of NaOH was consumed, but 50% of starting material was recovered.

A suspension of silver oxide (from 850 mg. of AgNO<sub>3</sub>) in 150 ml. of 50% aqueous dioxane containing 381 mg. of VIII was stirred in the dark at room temperature. Repeated ultraviolet spectra revealed a decrease to 60% of the original absorbance over 65 hr., with no other detectable change. From this, 190 mg. of VIII was isolated as the only well-defined organic product.

A solution of 365 mg. of X and 486 mg. of triethylamine in 40 ml. of acetonitrile was allowed to stand at room temperature for 6 days. Work-up with water and ether afforded recovered X (268 mg., 73%), m.p. 149– 150°, and a dark residue.

Potassium t-butoxide (236 mg., 2.1 mmoles) was added to a solution of the iodo compound X (700 mg., 2.09 mmoles) in 25 ml. of dimethyl sulfoxide. After 2 min. the mixture was poured into 100 ml. of ice water, producing a brown, turbid suspension. Ether extraction yielded recovered X (95 mg., m.p. 148–149°) and brown oils. Repeated chromatography produced no well-defined products. The aqueous solution was acidified with HNO<sub>3</sub>, then AgNO<sub>3</sub> was added, and silver iodide was collected, washed, and dried (298 mg., 62%). It was completely soluble in aqueous NaCN. Two other runs, also with careful chromatography, yielded no well-defined products, but only black tars.

1-Dimethylamino-2-nitro-3-phenyl-4-( $\alpha$ -hydroxybenzyl)cyclobutene (XI). A mixture of VI (437 mg., 2 mmoles) and purified benzaldehyde (360 mg., 3 mmoles) in 10 ml. of dimethyl sulfoxide was shaken for 10 min. after addition of ca. 20 mg. of potassium t-butoxide. The solution was poured into 150 ml. of water and the precipitate was washed with 10 ml. of methanol to give 320 mg. (49%) of crude XI, m.p. 191-193°, raised to 193-194° dec. on recrystallization from aqueous acetone.

*Anal.* Calcd. for  $C_{19}H_{20}N_2O_3$ : C, 70.35; H, 6.22; N, 8.34. Found: C, 70.30; H, 6.41; N, 8.07.

The infrared spectrum showed the expected bands, including those at 3.0 (OH) and 6.0  $\mu$  (C=C). The ultraviolet spectrum had  $\lambda_{max}$  376 m $\mu$  (log  $\epsilon$  4.26).

A similar condensation with *p*-nitrobenzaldehyde afforded 1-dimethylamino-2-nitro-3-phenyl-4- $(\alpha$ -hydroxy-*p*-nitrobenzyl)cyclobutene, m.p. 205–206° dec.

Anal. Calcd. for  $C_{19}H_{19}N_3O_5$ : C, 61.78; H, 5.19; N, 11.38. Found: C, 61.35; H, 5.30; N, 11.16.

The ultraviolet and infrared spectra were as expected.

*1-Dimethylamino-2-nitro-3-phenyl-4-benzylidenecyclobutene* (XII). A solution of 2.136 g. (6.6 mmoles) of XI and 6.25 g. (33 mmoles) of *p*-toluenesulfonyl chloride in 60 ml. of pyridine was heated to reflux for 10 min., then cooled and poured into 300 ml. of ice water. A dark green precipitate (1.3 g., m.p. 155-160° dec.) was collected and chromatographed on 250 g. of silica gel with 1:1 CH<sub>2</sub>Cl<sub>2</sub>-ether, affording 760 mg. (38%) of XII, m.p. 184-186°, on crystallization from CH<sub>2</sub>Cl-CH<sub>3</sub>OH.

Anal. Calcd. for  $C_{19}H_{18}N_2O_2$ : C, 74.49; H, 5.92; N, 9.15. Found: C, 74.30; H, 6.00; N, 9.21.

In the ultraviolet the compound had  $\lambda\lambda_{max}$  422 m $\mu$  (log  $\epsilon$  4.22) and 333 m $\mu$  (log  $\epsilon$  3.93). The infrared spectrum had the expected bands, including bands at 6.05 and 6.19  $\mu$ , while the n.m.r. spectrum showed a ten-proton multiplet at  $\delta$  7.27, a one-proton singlet at 7.13, a one-proton singlet at 4.88, and a six-proton singlet<sup>14</sup> at 3.54.

When 65 mg. (0.361 mmole) of N-bromosuccinimide was added to 100 mg. (0.327 mmole) of the benzylidene compound XII in 20 ml. of  $CH_2Cl_2$ , the solution rapidly changed from yellow to light green. Removal of the solvent and crystallization from  $CH_2Cl_2$ - $CH_3OH$  afforded 50 mg. of an *adduct* of N-bromosuccinimide to XII, m.p. 187–189° dec.

Anal. Calcd. for  $C_{23}H_{22}BrN_2O_4$ : C, 57.03; H, 4.58; Br, 16.50; N, 8.68. Found: C, 56.65; H, 4.50; Br, 16.61; N, 8.37.

The infrared spectrum showed bands at 5.60, 5.82, and  $6.02 \mu$  among others.

*I-Dimethylamino-2-nitro-3-phenyl-4-benzoylcyclobu*tene (XIII). A solution of 3.00 g. (9.24 mmoles) of XI in 60 ml. of pyridine was added to 2.87 g. (28.7 mmoles) of  $CrO_3$  in 100 ml. of pyridine, and the mixture was heated at 37° for 30 min. Then 10 ml. of methanol was added, the mixture was evaporated to dryness at room temperature *in vacuo*, and the residue was extracted with  $CH_2Cl_2$ . Chromatography of the organic material on 300 g. of silica gel afforded 2.9 g. of the crude ketone. Two recrystallizations from methanol yielded 0.7 g. (24%) of pure XIII, m.p. 134–135°. Anal. Calcd. for  $C_{19}H_{18}N_2O_3$ : C, 70.79; H, 5.63; N, 8.69. Found: C, 70.94; H, 5.84; N, 8.50.

In the ultraviolet the compound had  $\lambda_{max}$  370 mµ (log  $\epsilon$  4.27), while the infrared spectrum was similar to that of XI except that the OH band at 2.90 µ was missing and a new peak had appeared at 5.97 µ in addition to the band at 6.05 µ. The n.m.r. spectrum showed ten phenyl protons as a multiplet near  $\delta$  7.5, two cyclobutene protons as doublets at 4.92 and 3.93 (J = 1.8c.p.s.), and two nonequivalent N-methyl groups<sup>14</sup> at 3.8 and 2.77.

1-Dimethylamino-2-nitro-3-phenyl-4-benzoyl-4-bromocyclobutene (XIV) and 1-Benzoyl-1-bromo-2-dimethylamino-3-nitro-4-phenylbutadiene (XV). A solution of 215 mg. (1.35 mmoles) of Br<sub>2</sub> in 22 ml. of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to an ice-cold solution of 426 mg. (1.33 mmoles) of XIII in 40 ml. of  $CH_2Cl_2$  and 3.9 g. (48.8 mmoles) of pyridine. After 10 min. of stirring the solution was washed, dried, and evaporated at room temperature in vacuo. Crystallization from methanol afforded 290 mg. of a mixture of XIV and XV, m.p. 129-135° dec. A solution of 130 mg. of this mixture was refluxed for 2 hr. in 20 ml. of ethyl acetate, which was then concentrated to 5 ml. and cooled rapidly. The first crop was 65 mg. of dark red crystals of the open-chain isomer XV, m.p. 135-138° dec.

Anal. Calcd. for  $C_{19}H_{17}BrN_2O_3$ : C, 56.87; H, 4.27; Br, 19.92; N, 6.98; mol. wt., 401. Found: C, 56.85; H, 4.42; Br, 20.67; N, 7.05; mol. wt. (osmometer, benzene), 407.

The infrared spectrum (KBr) showed bands at 3.29, 3.40, 6.14 (s), 6.25 (w), 6.36 (w), 6.45 (s), 6.60 (s), and 6.94 (m)  $\mu$ , and numerous peaks above 7  $\mu$ . The ultraviolet spectrum (150 sec. after solution in ethanol) showed  $\lambda\lambda_{max}$  325 m $\mu$  (log  $\epsilon$  4.11) and 250 m $\mu$  (log  $\epsilon$  4.0).

A solution of 100 mg. of the mixture of XIV and XV in a few drops of  $CH_2Cl_2$  was diluted with 5 ml. of  $CCl_4$ . On cooling a first crop of the mixture was deposited and, on evaporation (0°) to 2 ml. and standing at  $-20^\circ$ , 55 mg. of pure XIV, the yellow cyclobutene isomer, was deposited, m.p. 130–132° dec.

Anal. Calcd. for  $C_{19}H_{17}BrN_2O_3$ : C, 56.87; H, 4.27; Br, 19.92; N, 6.98. Found: C, 56.92; H, 4.42; Br, 20.81; N, 7.12.

In the infrared (KBr) the compound showed bands at 3.30, 3.45, 5.98 (shoulder), 6.02 (s), 6.29 (w), 6.35 (w), 6.72 (w), and 6.95 (s)  $\mu$ , and peaks above 7  $\mu$ . In the ultraviolet spectrum (80 sec. after solution in ethanol) it had  $\lambda\lambda_{max}$  380 m $\mu$  (log  $\epsilon$  4.18) and 250 m $\mu$ (log  $\epsilon$  4.00).

When the ethanol ultraviolet solutions were allowed to stand at room temperature for several hours, they ultimately showed the same spectrum,  $\lambda_{max}$  380 m $\mu$ with a small shoulder at 325 m $\mu$ , starting from either XIV or XV. Kinetic studies with graphical solution of the rate equations showed  $k_{XIV} \rightarrow _{XV} = 3.5 \times 10^{-3}$ min.<sup>-1</sup> and  $k_{XV} \rightarrow _{XIV} = 11.2 \times 10^{-3}$  min.<sup>-1</sup>. Infrared spectra of CH<sub>2</sub>Cl<sub>2</sub> solutions of XIV or XV showed the same equilibration. In the n.m.r. spectrum of an equilibrated (several hours) solution in CH<sub>2</sub>Cl<sub>2</sub> at  $-20^{\circ}$ , there were phenyl protons at  $\delta$  7.47, the benzylic proton of XIV at 4.66, the N-methyls<sup>14</sup> of XIV at 3.80 and 3.23, and the N-methyl<sup>14</sup> protons of XV at 3.15 and 2.58. From the ratio of the N-methyl protons the ratio of XIV to XV at  $-20^{\circ}$  was 9:1. Rapid heating to  $+70^{\circ}$  caused coalescence<sup>14</sup> of the N-methyl peaks in each compound, leading to two broad peaks at  $\delta$  3.50 and 2.66. Heating for 2 hr. caused a decrease in the  $\delta$  3.50 band in favor of the 2.66 band. At room temperature, the equilibrium ratio of  $\delta$  3.50 to 2.66 was about 3:1, in agreement with the ratio of rate constants from the ultraviolet equilibrations above.

Treatment of the Mixture of XIV and XV with Base. A solution of 104 mg. of the mixture of XIV and XV in 7 ml. of acetonitrile with 3 ml. of triethylamine and 5 ml. of furan was allowed to stand at room temperature in the dark for 5 days, at which time  $\lambda_{max}$  shifted from 378 to 358 m $\mu$ . Aqueous work-up afforded 75 mg. of brown tar; addition of silver nitrate to the acidified aqueous solution afforded *ca*. 30 mg. of crude AgBr (theoretical 20 mg.). Chromatography of the brown tar on silica gel afforded 10 mg. of XIII, m.p. 133-135° dec., as the only defined product. A similar reaction for 20 hr. afforded 30 mg. of XIII, m.p. 130-133° dec., and 28 mg. of a mixture of XIII and XIV (and XV), identified by infrared spectra, m.p. 128-129°.

1-Dimethylamino-2-nitro-3-phenylcyclobuten-4-one (XVII). A warm solution of 1.560 g. (4.54 mmoles) of the iodo compound X in 35 ml. of acetonitrile was poured into 6.00 g. (35.5 mmoles) of silver nitrate and 1.43 g. (18.1 mmoles) of pyridine in 10 ml. of acetonitrile; a yellow precipitate formed immediately. After 45 min. of stirring at room temperature in the dark, the silver iodide was collected, washed, and dried, yielding 1.006 g. (94%). The filtrate was poured into ice water and the resulting precipitate was recrystallized from methanol, affording 1.111 g. (88%) of 1-dimethylamino-2-nitro-3-phenylcyclobutenyl 4-nitrate (XVIII), m.p. 106–108° dec. Anal. Calcd. for  $C_{12}H_{13}N_3O_5$ : C, 51.61; H, 4.69; N, 15.05. Found: C, 51.68; H, 4.90; N, 14.59.

The infrared spectrum showed peaks at 6.0, 6.9, 7.2, 7.7, etc.  $\mu$ , while the ultraviolet spectrum had  $\lambda_{\text{max}}$  372 (log  $\epsilon$  4.26). The n.m.r. spectrum showed a sharp five-proton peak at  $\delta$  7.58, two one-proton apparent singlets at 5.43 and 4.28, and two broad<sup>14</sup> (half-width: 10 c.p.s.) three-proton bands at 3.67 and 3.12.

A solution of 1.000 g. (3.58 mmoles) of the above nitrate in 25 ml. of acetonitrile with 2.424 g. (22.6 mmoles) of 2,6-lutidine was heated at reflux for 2 hr. The mixture was poured into 100 ml. of water containing 1.36 g. (22.6 mmoles) of acetic acid, and the product was collected in the usual way with methylene chloride. Chromatography on silica gel afforded the ketone XVII in the first benzene eluate, 162 mg. (19.5%), m.p.  $85-86^{\circ}$  from petroleum ether. It was recrystallized from benzene-petroleum, m.p.  $86.5-87.5^{\circ}$ .

Anal. Calcd. for  $C_{12}H_{12}N_2O_3$ : C, 62.20; H, 5.21; N, 12.06. Found: C, 62.22; H, 5.39; N, 11.80.

In the infrared (KBr) the compound showed strong bands at 5.67 and 6.00  $\mu$ . The ultraviolet spectrum had  $\lambda_{max}$  403 m $\mu$  (log  $\epsilon$  4.04). In the n.m.r. (CCl<sub>4</sub>) there was a five-proton sharp band at  $\delta$  7.19, a oneproton singlet at 4.78, and a broad six-proton band<sup>14</sup> at 3.35. In CH<sub>2</sub>Cl<sub>2</sub> the latter was split into two broad peaks<sup>14</sup> at  $\delta$  3.44 and 3.27, while in pyridine the two NCH<sub>3</sub> peaks<sup>14</sup> were separated by 16 c.p.s.

When a few drops of  $D_2O$  were added to the pyridine n.m.r. solution (external TMS standard) the CH band at  $\delta$  4.4 and the two NCH<sub>3</sub> groups at  $\delta$  2.65 and 2.40 decreased over 1–2 hr. at the same rate, apparently in favor of singlets at  $\delta$  5.05 and 2.25 (in an area ratio of 1:3.7), respectively. The n.m.r. spectrum of XVII in CS<sub>2</sub> was unchanged by 3 days of shaking with D<sub>2</sub>O.

## Isomerization of Biscyclopropenyls to Benzenes<sup>1,2</sup>

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Reduction of triphenylcyclopropenyl cation (I) with zinc affords a dimer, bistriphenylcyclopropenyl (II). The dimer does not dissociate to triphenylcyclopropenyl radical, but on heating, irradiation, or treatment with potassium amide it rearranges to hexaphenylbenzene. Reduction of ethyldiphenylcyclopropenyl cation (V) yields a dimer (VI) which rearranges on heating to a mixture of 1,2-diethyltetraphenylbenzene (VII) and 1,4diethyltetraphenylbenzene (VIII). Reduction of diphenylcyclopropenyl cation (III) affords directly 1,2,4,5tetraphenylbenzene (IV); the desired dimer IX was prepared by an alternate route. As part of the structure proof, IX was converted to a cyclopropenyl cation XI. On heating at 135° IX is converted to 1,2,4,5-tetraphenylbenzene (IV) and 1,2,3,4-tetraphenylbenzene (XII) in a ratio of 10:1. At 300°, the rearrangement gives a IV/XII ratio of 3.5. Photochemical rearrangement of IX reverses the ratio: XII/IV = 2.2; potassium amide rearranges IX to XII. Mechanisms to explain these results involve, for the thermal and photochemical reactions, progression through Ladenburg and Dewar benzene structures.

With the finding of aromatic stability in cyclopropenyl cations, it became of interest to examine the three

<sup>(1)</sup> Work on dimer II has been reported in a preliminary communication: R. Breslow and P. Gal, J. Am. Chem. Soc., 81, 4747 (1959). The work on dimer IX and its rearrangement, as evidence for path 3, was reported at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, and by R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

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