

pH Measurements were made using Beckman model G pH meters. These instruments were standardized before use with commercial certified buffer solutions.

**Procedures.**—Peroxonophosphoric acid was prepared for each kinetic run by acid hydrolysis of  $\text{Na}_4\text{P}_2\text{O}_8$  as follows: To 20.0 ml. of 0.10 *M*  $\text{Na}_4\text{P}_2\text{O}_8$  in a test-tube was added 2.00 ml. of 6.00 *M*  $\text{HClO}_4$ . The resulting solution was heated for 35 min. in an oil-bath at 50°. Under these conditions 60 to 70% of the peroxodiphosphate was hydrolyzed to peroxomonophosphoric acid. The remainder of the total active oxygen was present predominantly as peroxodiphosphoric acid with only a small concentration of  $\text{H}_2\text{O}_2$  (<1% of the total active oxygen). The solution was then cooled rapidly to about 35° and, noting zero time, added to a polyethylene reaction vessel which contained a known volume of quenching solution. The vessel was immediately placed in a constant temperature bath at  $35.8 \pm 0.05^\circ$ . The quenching solution contained a known amount of standard sodium hydroxide (to neutralize the acidity of the hydrolysis mixture and to fix approximately the pH of the resulting solution), a known amount ( $\sim 10^{-4}$  *M*) of either EDTA or  $\alpha, \alpha'$ -dipyridyl and, in some instances, a known volume of buffer solution.

Aliquots of the reaction solutions were withdrawn at appropriate time intervals and analyzed iodometrically for peroxomonophosphoric acid. Because of the considerable concentration of peroxodiphosphate present, the analyses were carried out in acetate buffers at pH 4.6; no interference from the oxidation of iodide ion by peroxodiphosphate was noted at this pH.

The decompositions of  $\text{CH}_3\text{CO}_3\text{H}$ ,  $\text{ClCH}_2\text{CO}_3\text{H}$  and  $\text{H}_2\text{O}_2$  were started by adding the required volume of peracid or peroxide solution to a buffer or NaOH solution, of the required pH, to which EDTA ( $\sim 10^{-3}$  *M*) had been added. As previously, aliquots were withdrawn by pipet periodically and analyzed, the analyses for  $\text{CH}_3\text{CO}_3\text{H}$  and  $\text{ClCH}_2\text{CO}_3\text{H}$  being carried out in phosphate buffers of pH 3.5.

The prepared *t*-BuOOH solutions were immersed in a constant temperature water-bath and aliquots taken at intervals of 24 hr. and analyzed by an iodometric method.<sup>22</sup>

The pH of all reaction solutions was measured at the start and at the end of a kinetic run. In buffered solutions the pH was usually constant to  $\pm 0.1$  pH unit.

Samples, for mass spectrometric analysis, of the oxygen evolved in the base-catalyzed decomposition of the labeled peroxyacetic acid were collected as follows: 5 ml. of labeled  $\text{CH}_3\text{CO}_3\text{H}$  solution was added to the side arm of a 100-ml. reaction vessel. Contained within the same flask was 45 ml. of a carbonate buffer solution ( $\sim 10^{-3}$  *M* in EDTA) which maintained a pH near 8.2, the  $pK_a$  of peroxyacetic acid. The purity

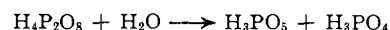
of this buffer had been previously determined by following the spontaneous decomposition of ordinary peroxyacetic acid.

The reaction flask and its contents were then attached to a vacuum line and thoroughly flushed with a stream of prepurified nitrogen. After passage of nitrogen gas for at least 1 hr., a sample was taken from above the liquids, and the nitrogen flow terminated. Mass spectral analysis of the blank sample demonstrated the efficiency of this process. Following this the reaction vessel was turned into a position enabling the two liquids to mix. After a period corresponding to ca. 70% reaction, a representative sample of gas (now nitrogen and oxygen) was taken.

The remaining 0.4-ml. portion of the hydrogen peroxide used initially to prepare the labeled peroxyacetic acid was diluted with 9.6 ml. of de-ionized water. One-half of this solution was oxidized with an excess of acid ceric ion in the same apparatus and according to the same procedure used for the spontaneous decomposition.

A repeat of this experiment was carried out with the remaining  $\text{H}_2\text{O}_2$  solution. Since it is known<sup>23,24</sup> that the O—O bond of  $\text{H}_2\text{O}_2$  is not broken on oxidation by an excess  $\text{Ce(IV)}$ , these experiments gave the relative amounts of  $\text{H}_2\text{O}_2$ <sup>16,16</sup>,  $\text{H}_2\text{O}_2$ <sup>16,18</sup> and  $\text{H}_2\text{O}_2$ <sup>18,18</sup>. It was assumed that the  $\text{CH}_3\text{CO}_3\text{H}$  was labeled in the same relative amounts.<sup>25</sup>

A spectrophotometric method<sup>26</sup> was used to evaluate the acid dissociation constants of  $\text{H}_3\text{PO}_5$ . Potentiometric titration, used to determine the acid dissociation constants of  $\text{CH}_3\text{CO}_3\text{H}$  and  $\text{ClCH}_2\text{CO}_3\text{H}$ , could not be used since an equimolar mixture of peroxomonophosphoric and phosphoric acids is obtained on acid hydrolysis of peroxodiphosphate, according to the equation



**Acknowledgment.**—The authors wish to thank the U. S. Atomic Energy Commission (contract No. AEC-1983) for their continued financial support. Acknowledgment is also due to Drs. G. O. Dudek and T. G. Traylor for the mass spectral analysis and to Dr. H. C. Kelly for helpful discussions.

(24) C. A. Bunton and D. R. Llewellyn, *Research*, **5**, 142 (1952); A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952); S. Baer and G. Stein, *J. Chem. Soc.*, 3176 (1953); P. B. Sigler and B. J. Masters, *J. Am. Chem. Soc.*, **79**, 6353 (1957).

(25) C. A. Bunton, T. A. Lewis and D. R. Llewellyn, *J. Chem. Soc.*, 1226 (1956).

(26) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

[CONTRIBUTION No. 1725 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

## Polyoxomethylene Small-Ring Hydrocarbons: Tetramethylenecyclobutane and Dihydratetramethylenecyclobutane<sup>1</sup>

By G. W. GRIFFIN AND L. I. PETERSON<sup>2</sup>

RECEIVED MARCH 12, 1963

Tetramethylenecyclobutane (I), a cross-conjugated hydrocarbon of theoretical interest, has been synthesized by two independent routes. Although non-isolable, it is stable in dilute solutions to both acid and base and has been characterized by spectral analysis as well as by chemical evidence. By classical standards compound I cannot be considered aromatic although it is indefinitely stable in dilute solution at  $-78^\circ$  in the absence of oxygen. Its marked sensitivity to oxygen and tendency to polymerize may be rationalized in theoretical terms. In relation to our work with I, the synthesis of dihydratetramethylenecyclobutane (XII) has also been achieved.

A variety of small carbocyclic systems possessing one or more double bonds exocyclic to the ring have been synthesized during the past decade. In the cyclobutane series, representative examples having one, two and three exomethylene groups have been reported.<sup>3</sup> The present study was initiated in order to determine whether tetramethylenecyclobutane which, like cyclo-

butadiene, possesses four such  $sp^2$ -hybridized carbon atoms in the ring would be capable of even precarious independent existence.<sup>4</sup> We were encouraged in this endeavor by earlier predictions based on simple Hückel-MO calculations which indicated that in contrast to cyclobutadiene a singlet ground state, as well as a substantial delocalization energy (1.67  $\beta$ ), might be anticipated for I.<sup>5</sup> In order to translate the calculated

(1) For a preliminary communication on this subject, see G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 3398 (1962).

(2) Procter and Gamble Predoctoral Fellow, 1962-1963.

(3) (a) J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4269 (1959); (b) A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955); (c) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); (d) F. F. Caserio, Jr., S. H. Parker, R. Piccolini and J. D. Roberts, *ibid.*, **80**, 5507 (1958); (e) M. P. Cava, M. J. Mitchell and R. J. Pohl, *Tetrahedron Letters*, **No. 18**, 825 (1962); (f) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).

(4) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(5) While our work was in progress a compound related to I, namely, octaphenyltetramethylenecyclobutane, was obtained by photodimerization of 1,1,4,4-tetraphenylbutatriene; R. O. Uhler, H. Shechter and G. V. D. Tiers, *ibid.*, **84**, 3397 (1962).

A substituted tetramethylenecyclobutane structure was also considered for a  $\text{C}_{20}\text{H}_{28}$  hydrocarbon formed when ascaridole is heated in *p*-cymene, although no experimental evidence other than molecular weight and carbon-

delocalization energy into the hypothetical resonance energy, it is necessary to evaluate the destabilization due to strain. However, on the basis of published thermochemical data, it would be difficult to estimate with any degree of certainty the strain which would accumulate on introducing four trigonal centers into the already strained cyclobutane ring.<sup>6</sup> In the absence of direct experimental evidence, it remained to be established experimentally whether the delocalization energy would be sufficient to compensate for the presumed adverse effects of strain.

In spite of the favorable predictions with regard to electron delocalization and ground state multiplicity, the free valency index calculated for the termini of I is substantial (0.88). For comparison, the predicted index for *p*-xylylene is 0.92 and while the latter is stable in the gas phase it undergoes rapid polymerization in solution.

Aside from verifying theoretical predictions the synthesis of I also would afford a potential precursor for a number of substituted cyclobutadienes as well as a simple, highly symmetrical molecule to employ for a variety of spectral studies. Especial interest is attached to the possibility of detecting 1,3-cross ring  $\pi$ -electronic interaction in this system.<sup>3d</sup>

Photodimers of fumaric acid derivatives such as fumaronitrile, fumaramide<sup>7</sup> and dimethyl fumarate provide ideal precursors for tetramethylenecyclobutane. Of these, the dimer of dimethyl fumarate, namely, *cis,trans,cis*-1,2,3,4-tetracarboxymethylcyclobutane has emerged as the most attractive starting material from a synthetic standpoint since it is obtained in excellent yield and high purity and possesses the chemically versatile carbomethoxy group.

The synthesis of tetramethylenecyclobutane was initially achieved in yields of 1–2% by the thermal decomposition of *cis,trans,cis*-1,2,3,4-tetra-(dimethylaminomethyl)-cyclobutane tetraoxide (II) at 250° in a nitrogen atmosphere under reduced pressure. The preparation of this precursor for I has been described in a previous paper.<sup>8</sup> The effluent gases from the

hydrogen analysis was presented in support of the admittedly tentative assignment; see, H. Thoms and W. Dobke, *Arch. Pharm.*, **268**, 128 (1930). We have shown that this hydrocarbon is, in reality, bis-*p*-cymene (C<sub>20</sub>H<sub>26</sub>), formed by solvent oxidation.

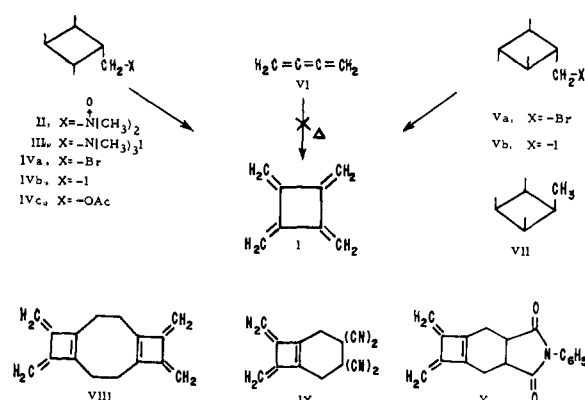
(6) Estimation of the total  $\sigma$ - and  $\pi$ -strain in I appears virtually impossible on the basis of the relatively few and apparently contradictory thermochemical data available for related systems. The heat of isomerization of methylenecyclobutane with one trigonal center to 1-methylcyclobutene (based on heats of hydrogenation and corrected for degree of substitution) is endothermic by a mere 0.6 kcal./mole in spite of the fact that the latter possesses two sp<sup>2</sup>-ring atoms. Furthermore, a third trigonal center apparently introduces very little additional strain as indicated by the heat of isomerization of 1,3-dimethylenecyclobutane to its endocyclic isomer 1-methyl-3-methylenecyclobutene (R. B. Turner, "Theoretical Organic Chemistry," Kekulé Symposium, London, Butterworth Scientific Publications, 1958, p. 75). Krall and Roberts also report that the variation in the number of sp<sup>2</sup>- and sp<sup>3</sup>-carbon atoms in the four-membered ring of compounds such as 3-phenylcyclobutanone and 3-phenylcyclobutanone does not change the angular strain more than the uncertainty in their determinations (R. E. Krall and J. D. Roberts, *Am. Chem. Soc., Div. Petrol. Chem., Symp.*, **3**, No. 4B, 63 (1958)). Extrapolation of these observations leads to the intuitively unreasonable result that the strain energy of I should not differ markedly from that of methylenecyclobutane or for that matter cyclobutane itself (~27 kcal./mole). On the other hand, reliable experimental data on biphenylene with four trigonal atoms in a four-membered ring indicate that the strain is substantial (59 ± 5 kcal./mole) (R. C. Cass, H. D. Springall and P. G. Quincey, *J. Chem. Soc.*, 1188 (1955)). The theoretical estimate of 50–60 kcal./mole for the strain energy of cyclobutadiene is in accord with these observations (W. Weltner, Jr., *J. Am. Chem. Soc.*, **75**, 4224 (1953)).

(7) The photodimerization of fumaramide to give the *cis,trans,cis*-dimer (40%) was achieved by irradiation of a stirred suspension of 20 g. of fumaramide in 200 ml. of water for 6 days. A Westinghouse 15T8 germicidal sterilamp was employed as a light source. Recrystallization from water gave white crystals, m.p. > 310°. The stereochemistry was established by acidic hydrolysis and subsequent esterification with diazomethane to give *cis,trans,cis*-1,2,3,4-tetracarboxymethylcyclobutane.

(8) G. W. Griffin, J. E. Basinski and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).

pyrolysis were trapped in hexane maintained at -78°. The basic materials were removed by washing with dilute hydrochloric acid and the product was separated from polymers and incompletely pyrolyzed starting material by codistillation with hexane at 0° under vacuum. A temperature of 250° is required in order to avoid incomplete decomposition of the amine oxide; however, excessive destruction of the product appears to occur if the temperature is elevated above this point. The product prepared according to this procedure is obtained free of benzenoid hydrocarbons which conceivably might arise from thermal reorganization and subsequent aromatization. This is in sharp contrast to the results obtained on pyrolysis of *cis,trans,cis*-1,2,3,4-tetraacetoxymethylcyclobutane (IVc).

CHART I



Perhaps the most characteristic chemical property of I is its marked sensitivity to oxygen. On brief exposure to air, it forms intractable products containing up to 40% oxygen. Tetramethylenecyclobutane was found to be remarkably stable, however, to dilute mineral acids and strong bases. All reactions and physical measurements on I were conducted in dilute solutions under a nitrogen blanket in order to avoid oxidation and polymer formation.

Pyrolysis of the Hofmann base III<sup>8</sup> under analogous, albeit milder, conditions (115°) also afforded the desired tetraene I. The product obtained in this manner was contaminated with an artifact produced in the Hofmann elimination. Spectral evidence indicates that this by-product possesses a dimethylenecyclobutene structure.

The elimination of four moles of hydrogen halide from a variety of 1,2,3,4-tetrahalomethylcyclobutanes<sup>9a</sup> of different stereochemistry represents by far the most convenient synthetic route to I. For example, *trans,trans*-1,2,3,4-tetrabromomethylcyclobutane (Va) reacts at 0° with sodium ethoxide in ethanol to give tetramethylenecyclobutane in greater than 50% yield. The product was separated from sodium bromide and residual sodium ethoxide by codistillation with ethanol under reduced pressure.

The thermal dimerization of 1,2,3-butatriene<sup>10</sup> appeared to be an attractive potential synthetic route to tetramethylenecyclobutane. The corresponding reaction with allenes is apparently general and affords

(9) A. F. Velturo, Ph.D. Dissertation, Yale University, New Haven, Conn., 1962. The pyrolysis of *cis,trans,cis*-1,2,3,4-tetraacetoxymethylcyclobutane at 540° gave a mixture of six hydrocarbons, namely, benzene, toluene, ethylbenzene, *o*-xylene, styrene, and anthracene (in the approximate ratio of 1:2:1:2:5:8, respectively).

(9a) NOTE ADDED IN PROOF.—The preparation and properties of the 1,2,3,4-tetrahalomethylcyclobutanes will be described in a subsequent communication.

(10) W. M. Schubert, T. H. Liddicoet and W. A. Lanka, *J. Am. Chem. Soc.*, **76**, 1929 (1954).

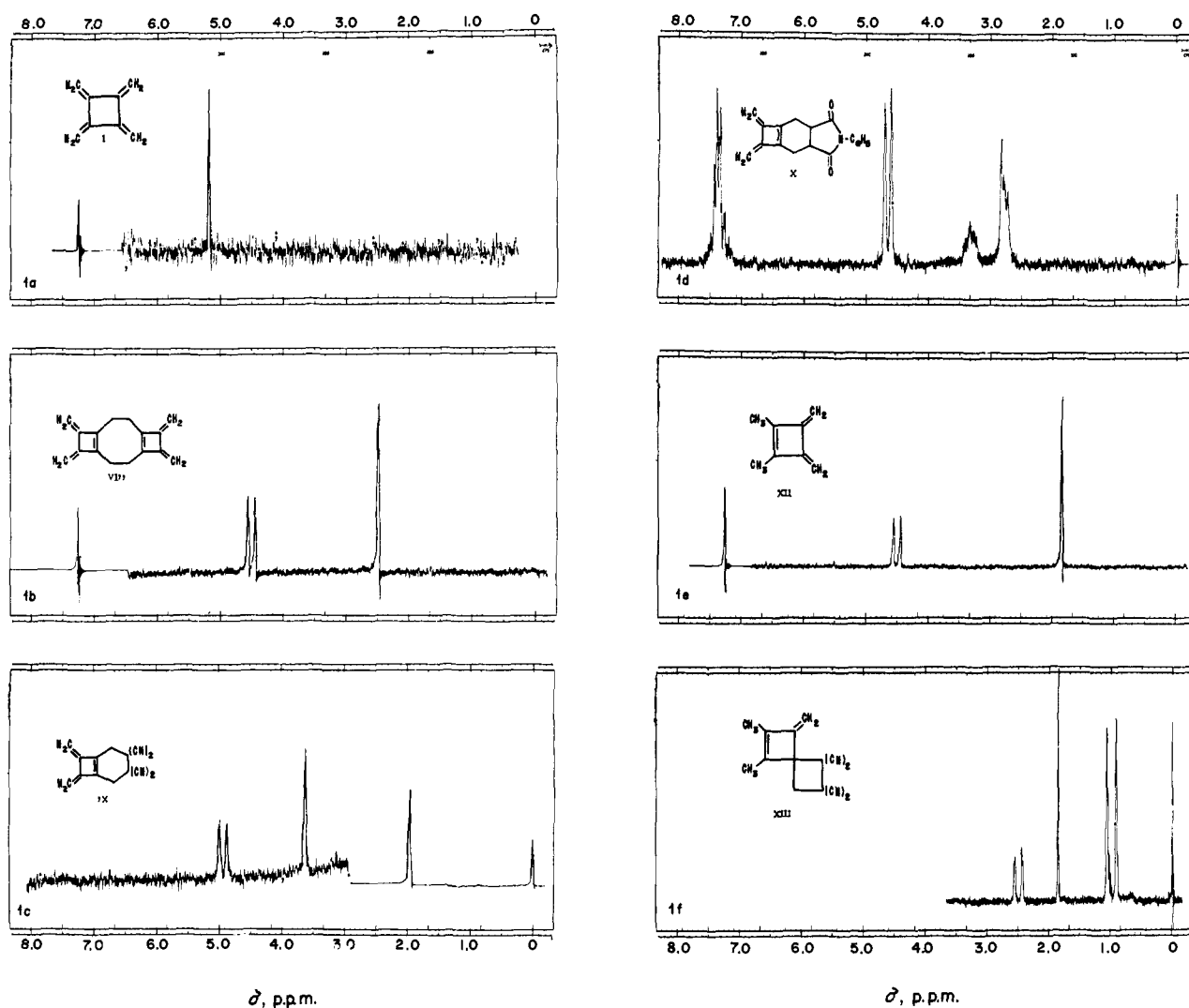


Fig. 1.—N.m.r. spectra of: 1-a, tetramethylenecyclobutane (I); 1-b, dimer of tetramethylenecyclobutane (VIII); 1-c, Diels-Alder adduct of I with tetracyanoethylene (IX); 1-d, Diels-Alder adduct of I with N-phenylmaleimide (X); 2-e, dihyrotetramethylenecyclobutane (XII); 1-f, 1,2-cyclo-adduct of XII with tetracyanoethylene (XIII). The spectra were obtained with a Varian A-60 spectrometer.  $\text{CHCl}_3$ , 1-a, 1-b, 1-e;  $\text{CH}_3\text{CN}$ , 1-c;  $\text{CDCl}_3$ , 1-d;  $\text{CD}_3\text{COCD}_3$ , 1-f.

1,2- and/or 1,3-dimethylenecyclobutanes.<sup>11</sup> Recently, 1,1,4,4-tetraphenylbutatriene has been shown to give octaphenyltetramethylenecyclobutane by a photochemical process.<sup>5</sup> Unfortunately, the passage of butatriene through a tube of Pyrex helices over a range of temperatures from 150–550° failed to yield even traces of I.

The following evidence may be cited in favor of the structural assignment to I: (1) The mass spectrum of I determined in hexane exhibited the expected peak at  $m/e$  104 (parent mass) not present in the spectrum of the solvent. The method of purification precludes the possibility that a species retaining an amine oxide group undergoes reaction in the mass spectrometer and is responsible for the observed peak. Data on the cracking pattern of I was not discernible because of the necessarily large excess of solvent employed.

(2) The infrared spectrum of a dilute solution of tetramethylenecyclobutane in carbon tetrachloride shows a sharp, intense peak at 880  $\text{cm}^{-1}$  which is near the characteristic region for hydrogen out-of-plane vibrations in terminal disubstituted olefins.<sup>12</sup> Other

characteristic bands in the infrared spectrum occur at 1400(m), 1760(w), 1710(w) and 3095(w)  $\text{cm}^{-1}$ . The weak, high-frequency band may be attributed to the exomethylene C–H stretching mode. When the carbon tetrachloride solution is allowed to stand for 12 hr. at room temperature the band at 880  $\text{cm}^{-1}$  is completely replaced by another intense band at 856  $\text{cm}^{-1}$ . The 856  $\text{cm}^{-1}$  peak, as is later shown, may be attributed to dimer formation.

(3) The n.m.r. spectrum of I in chloroform (Fig. 1a) consists of a single peak at  $\tau = 4.81$ . It should be noted that the signal produced by the exomethylene protons of a model system (dihyrotetramethylenecyclobutane (XII)) are observed at  $\tau = 5.45$ . The observed chemical shift of 0.7 p.p.m. might be attributed to electron delocalization and the resulting diamagnetic anisotropy of the cyclic  $\pi$ -electronic system, produced by ring currents.

(4) The elaborate ultraviolet spectrum of I in ethanol (Fig. 2) possesses a strong absorption maximum at 208  $m\mu$  ( $\epsilon$  49,500) in addition to six longer wave length maxima at 263 (1.40), 271 (1.54), 281.5 (1.40), 295.5 (0.84), 312 (0.25), 325 (0.08)  $m\mu$ . The figures in parentheses indicate the intensities relative to an "apparent"<sup>13</sup> maximum at 208 (10.00)  $m\mu$ . The long

(11) J. D. Roberts and C. M. Sharts, "Organic Reactions," Vol. XII, John Wiley and Sons, Inc., New York, N. Y., 1962, p. 23.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 51.

wave length maxima are separated by approximately  $1600\text{ cm.}^{-1}$ , which is near the value observed for the double bond absorption band in the infrared region. The minimum extinction coefficient for the  $208\text{ m}\mu$  peak was determined by assuming quantitative conversion of a weighed sample of *trans,trans,trans*-1,2,3,4-tetraiodomethylcyclobutane (Vb) to I.

As expected,<sup>14</sup> catalytic hydrogenation of I using platinum-on-charcoal catalyst gave exclusively *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane (VII). The infrared spectrum and g.l.p.c. retention time of the hydrogenation product were identical with those of a hydrocarbon obtained by Criegee<sup>15</sup> on catalytic reduction of *cis*-1,2,3,4-tetramethylcyclobutene and assigned the *cis,cis,cis* stereochemistry. The n.m.r. and mass spectra of VII are consistent with the designated structure.<sup>16</sup>

Tetramethylenecyclobutane is indefinitely stable in dilute solution at  $-78^\circ$ ; however, on warming to room temperature, it undergoes dimerization to a 1,5-cyclooctadiene. The apparently greater stability in the gas phase even at substantially higher temperatures is in accord with the theoretical free valence predictions. The infrared and ultraviolet spectra indicate the presence of a dimethylenecyclobutene moiety in the dimer. The n.m.r. spectrum (Fig. 1b) exhibits peaks at  $\tau = 5.45$ ,  $5.55$ , and  $7.52$ . The integrated intensities are in the ratio of 1:1:2, confirming the structural assignment as 5,6,11,12-tetramethylenetricyclo[8.2.0.0<sup>4,7</sup>]dodeca-1(10),4(7)-diene (VIII). Like I, this dimer is very sensitive to oxygen and on exposure to air is converted into a highly insoluble polymer.

Tetramethylenecyclobutane (I) formally may be regarded as a potential precursor for substituted cyclobutadienes. Conceivably, advantage might be taken of the Diels-Alder reaction in order to introduce endocyclic double bonds into the four-membered ring, although earlier attempts to achieve similar conversions have proven unsuccessful.<sup>3c,3f</sup> The reaction of I with tetracyanoethylene at  $0^\circ$  gave a colorless, relatively stable crystalline material isolated by chromatography on acid-washed alumina. The elemental analysis and ebullioscopic molecular weight indicate a 1:1 adduct. The ultraviolet spectrum determined in acetonitrile shows an absorption maximum at  $209\text{ m}\mu$  ( $\epsilon$  26,200) and a shoulder at  $246.5\text{ m}\mu$  ( $\epsilon$  4,090) characteristic of dimethylenecyclobutenes. The n.m.r. spectrum in acetonitrile (Fig. 1c) exhibits peaks at  $\tau = 5.13$ ,  $5.24$ , and  $6.45$ . The integrated areas are within experimental error of the expected ratio of 1:1:2, respectively. These

(13) "False energy" maxima arising from scattered light are known to appear in the region  $200\text{--}215\text{ m}\mu$  when spectra of simple monoolefins are determined on standard photoelectric spectrometers; see O. H. Wheeler and J. L. Mateos, *J. Org. Chem.*, **21**, 1110 (1956).

(14) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(15) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959). We are indebted to Professor Criegee for generous samples of *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane for infrared comparisons. Criegee's assignment of *cis* stereochemistry to VII rests on the application of the Auwers-Skita rule to the isomeric 1,2,3,4-tetramethylcyclobutenes. In turn the reduction product of *cis*-1,2,3,4-tetramethylcyclobutene was then assigned the "all-*cis*" stereochemistry on the assumption of *cis*-catalytic hydrogenation from the least hindered side. There appears to be no reason to question these assignments. Doering has recently confirmed that application of the Auwers-Skita rule to rigid small-ring systems leads to the correct conclusion with regard to stereochemistry. See W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(16) Difficulties were encountered in all attempts by hydrogenation to determine accurately the degree of unsaturation in I, because of problems associated with establishing accurately the concentration of the tetramethylenecyclobutane in dilute solution. Catalytic deuteration followed by mass spectral analysis was seen as a possible means of circumventing this problem. Unfortunately, all experiments in this direction were complicated by deuterium-hydrogen exchange. Similar exchange under a variety of solvent and catalyst conditions was noted in control experiments with cyclooctatetraene.

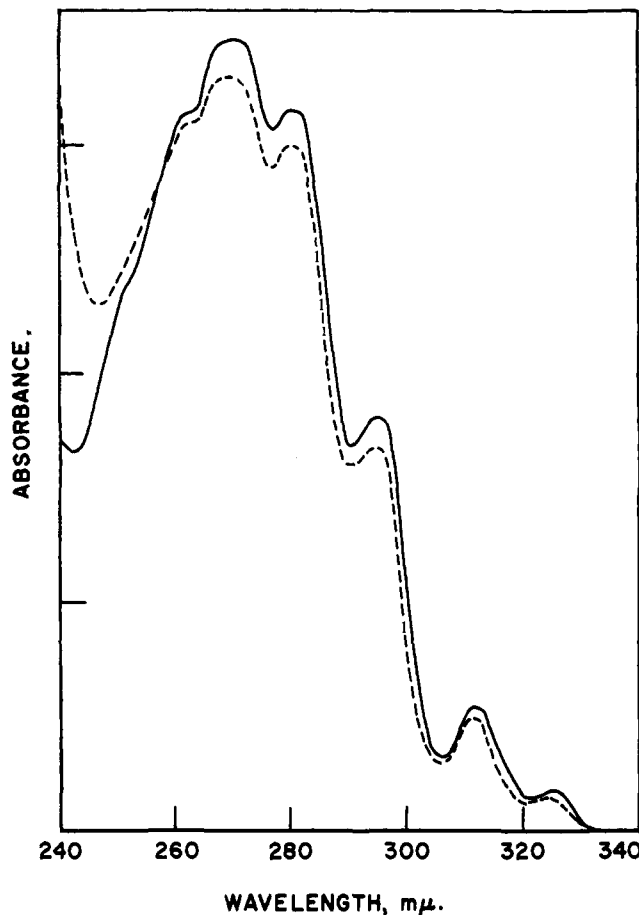


Fig. 2.—Ultraviolet spectra of tetramethylenecyclobutane generated from the amine oxide II (solid line, hexane) and the tetraiodide Vb (dashed line, ethanol). The scale on the ordinate has been omitted since exact concentrations are unknown.

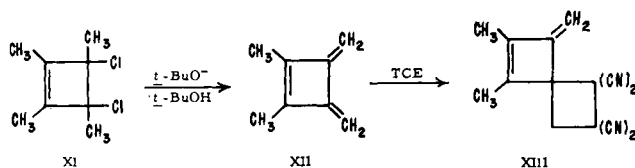
combined experimental data are uniquely accommodated by the mono-Diels-Alder adduct 3,3,4,4-tetracyano-7,8-dimethylenebicyclo[4.2.0]octa-1(6)-ene (IX). The latter undoubtedly represents the most stable dimethylenecyclobutene isolated to date. N-Phenylmaleimide may also be employed as a dienophile and provides the corresponding adduct X. The structure of X is supported by ultraviolet, n.m.r. (Fig. 1d), and infrared spectral evidence. Although a large excess of dienophile was employed in each case, no products resulting from addition of two moles of tetracyanoethylene or N-phenylmaleimide could be isolated. The reaction with tetracyanoethylene takes place at  $0^\circ$ , whereas with N-phenylmaleimide a slightly higher temperature ( $25^\circ$ ) is required. At  $0^\circ$  the reaction of N-phenylmaleimide with I is so slow that a competing reaction, namely, dimerization, becomes significant and nearly equal amounts of dimer and adduct are obtained.

Dihydrotetramethylenecyclobutane (XII) was of interest in connection with anticipated heat of hydrogenation studies on I and as another potential precursor for substituted cyclobutadienes. The synthesis of this new hydrocarbon<sup>17</sup> was achieved by dehydrochlorination of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (XI) with potassium *t*-butoxide. In the absence of oxygen the product possesses sufficient stability to be isolated by preparative scale g.l.p.c. procedures. The mass spectrum showed the parent mass at  $m/e$  106 and the base

(17) An independent synthesis of XII and its adduct with tetracyanoethylene was simultaneously achieved by Criegee and Dekker; see R. Criegee, *Angew. Chem.*, **74**, 703 (1962). That the products are identical has been confirmed by direct comparison of n.m.r. and infrared spectra: R. Criegee, private communication.

peak at  $m/e$  91 corresponding to the loss of a methyl group. The ultraviolet spectrum has two absorption maxima at 213  $m\mu$  (minimum  $\epsilon$  10,500) and at 249  $m\mu$  (minimum  $\epsilon$  3,530). Bands are observed at 3089(m), 1696(m), 1643(s), 1604(m) and 852 (vs)  $cm^{-1}$  in the infrared spectrum of XII. These data are very similar to those reported for the related 3,4-dimethylenecyclobutene<sup>3f</sup> and 1-methyl-3,4-dimethylenecyclobutene.<sup>3a</sup> Catalytic reduction of XII over palladium-on-charcoal gave *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane as the major product. The n.m.r. spectrum of dihydrotetramethylenecyclobutane determined in chloroform exhibits resonance at  $\tau = 5.44$  and 5.56 for the exomethylene protons and at  $\tau = 8.17$  for the methyl protons in the correct ratio of 1:1:3, respectively.

CHART II



The reaction of XII with tetracyanoethylene at 25° gave instead of the desired Diels-Alder adduct, a product which results from 1,2-cyclo-addition. Blomquist and Meinwald<sup>3c</sup> found that 1,2-diphenyl-3,4-dimethylenecyclobutene behaves in a similar fashion. The infrared and ultraviolet spectra suggest the presence of a methylenecyclobutene function. Elemental analysis and an ebullioscopic molecular weight determination established that the product was a 1:1 adduct. The n.m.r. spectrum displays signals at  $\tau = 4.90$  and 5.14 for two exomethylene hydrogens, at  $\tau = 6.30$  for two ring protons, and at  $\tau = 7.85$  and 8.17 for the two allylic methyl groups. These combined experimental observations are accommodated by structure XIII, 1,2-dimethyl-3-methylene-4,4,5,5-tetracyanospiro[3.3]hept-1-ene.

A correlation study of the observed gas phase ultraviolet spectrum of I with the theoretical spectrum is in progress and experiments designed to determine the heat content of the exomethylene groups relative to ordinary strain-free terminal disubstituted olefinic bonds are also contemplated. The synthetic techniques applied to the cyclobutyl derivatives described in this communication are currently being extended to related cyclopropyl systems.

### Experimental

**Synthesis of Tetramethylenecyclobutane (I). Method A. From the Amine Oxide II.**—*cis,trans,cis*-1,2,3,4-Tetra-(dimethylaminomethyl)-cyclobutane tetraoxide (II) (4.9 g., 0.014 mole) as a 50% aqueous solution was added dropwise over a 15-min. period to a dry Pyrex flask preheated to 250°. A nitrogen atmosphere was employed and the pressure was maintained at 1–5 mm. throughout the course of the pyrolysis. Two receivers connected in series each containing 5 ml. of *n*-hexane and cooled in a Dry Ice-acetone bath were used to collect the pyrolyzate. In all cases the thermal decomposition proceeded only with difficulty and the major part of the starting material was converted to a tarry residue which remained in the pyrolysis flask. Only traces of I could be detected when the pyrolysis temperature was varied by 25° from the apparently optimum temperature of 250°. The hexane solutions from the Dry Ice traps were combined, washed with 1 *N* hydrochloric acid to remove dimethylhydroxylamine produced during the pyrolysis reaction, then with 5% aqueous potassium carbonate, and finally dried over anhydrous potassium carbonate. The temperature of the solution was maintained at 0–4° during the washing procedure and extreme care was exercised in order to exclude oxygen. All transfers and extractions were conducted under a blanket of nitrogen. Separation of polymers and incompletely pyrolyzed material was accomplished by codistillation of the hexane solution of I at 0° (0.02 mm.). The yield was estimated from the ultraviolet absorption spectrum of the hexane solution (assuming  $\epsilon_{max}$  100,000 for  $\lambda_{max}$  208  $m\mu$ ) to be 1–2%. When exposed to air, compound I poly-

merized rapidly and gave intractable oxygen-containing polymers; however, dilute solutions could be stored at –78° under nitrogen for prolonged periods.

**Synthesis of Tetramethylenecyclobutane (I). Method B. From the Hofmann Base III.**—The thermal decomposition of *cis,trans,cis*-1,2,3,4-tetra-(trimethylammoniummethyl)-cyclobutane tetrahydroxide (III) at 115°, 200° and 250° under conditions otherwise identical to those employed for the amine oxide yielded tetramethylenecyclobutane (1%). That this product was identical to that obtained from the amine oxide II was established by comparison of spectral data. The product obtained from the Hofmann base III was contaminated with appreciable amounts of a neutral impurity. It is conceivable that this contaminant is a dihydrotetramethylenecyclobutane resulting from a side reaction in the Hofmann elimination. The presence of absorption at 245  $m\mu$  in the ultraviolet spectrum could be indicative of the dimethylenecyclobutene chromophore.

**Synthesis of Tetramethylenecyclobutane (I). Method C. By Dehydrohalogenation of Tetrahalomethylcyclobutanes.**—*trans,trans,trans*-1,2,3,4-Tetrabromomethylcyclobutane (Va, 0.70 g., 1.64 mmoles) was dissolved with stirring under a nitrogen atmosphere in 200 ml. of ethanol containing 6 g. (0.09 mole) of sodium ethoxide. The reaction temperature was maintained at 0° for 36 hr. The product was then separated from sodium bromide and excess sodium ethoxide by codistillation with ethanol at 0° (0.02 mm.). The ultraviolet absorption (assuming  $\epsilon$  100,000 for  $\lambda_{max}$  208  $m\mu$ ) indicated a 50% yield (0.084 g.) of tetramethylenecyclobutane. *trans,trans,trans*-1,2,3,4-Tetraiodomethylcyclobutane (Vb) as well as the corresponding isomeric *cis,trans,cis*-bromide IVa and iodide IVb was shown to undergo dehydrohalogenation under similar conditions to give I.

*trans,trans,trans*-1,2,3,4-Tetraiodomethylcyclobutane (Vb, 8.90 mg.,  $1.28 \times 10^{-6}$  mole) dissolved in 60.0 ml. of a dilute solution of sodium ethoxide in ethanol showed an extinction coefficient of 49,500 for the maximum at 208  $m\mu$ . This value was obtained by assuming quantitative conversion of the iodide to tetramethylenecyclobutane. Thus, this figure undoubtedly represents a lower limit.

**Catalytic Reduction of Tetramethylenecyclobutane (I).**—Twenty-five milliliters of a pentane solution containing approximately 10 mg. of tetramethylenecyclobutane was subjected to hydrogenation at 0° over 0.25 g. of 5% platinum-on-charcoal catalyst in a semimicro apparatus at atmospheric pressure. The hydrogen uptake was essentially complete after 2 min. The reaction mixture was then filtered and the pentane distilled utilizing a microdistillation column packed with glass helices. The remaining 0.5 ml. of solution was gas chromatographed on a Carbowax 20M preparative column and a product having the same retention time and infrared spectrum as *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane (VII) was isolated.<sup>16</sup> The n.m.r. spectrum of VII exhibits signals at  $\tau = 9.13$  and 7.50 with integrated areas in a 3:1 ratio. The mass spectrum with the expected parent mass at  $m/e$  112 and the base peak at  $m/e$  56 also supports the structural assignment. The infrared spectrum determined in carbon tetrachloride exhibits significant bands at 2971(vs), 2922(vs), 2880(s), 1465(m), 1450(m), 1388(m), 1372(m), 1015(m), 1000(m)  $cm^{-1}$ .

**Dimer of Tetramethylenecyclobutane (VIII).**—An ethanol solution (80 ml.) of tetramethylenecyclobutane generated from 1.0 g. (2.3 mmoles) of *trans,trans,trans*-1,2,3,4-tetrabromomethylcyclobutane (Va) was degassed and allowed to stand for 12 hr. at 25°. The progress of the reaction was followed by ultraviolet spectral analysis which indicated about 80% conversion to dimer after 12 hr. The solvent and unreacted monomer were removed under vacuum and the crude dimer was dissolved in 5 ml. of benzene. The resulting solution was chromatographed, with benzene, on acid-washed alumina. The first 75 ml. of eluent was lyophilized affording 45 mg. (19%, based on Va) of the colorless amorphous dimer. Care must be exercised at all times to avoid contact of the dimer with air since it reacts rapidly with oxygen. The ultraviolet spectrum (ethanol) showed an absorption maximum at 214  $m\mu$  with a shoulder at 245  $m\mu$ . The infrared spectrum (chloroform) exhibits absorption at 3090(m-w), 1699(m), 1640(s), 1576(m-s) and 856(vs)  $cm^{-1}$ , apparently characteristic of dimethylenecyclobutenes. The n.m.r. spectrum determined in chloroform with signals at  $\tau = 5.45$ , 5.55 and 7.52 in the integrated ratio of 1:1:2 is reproduced in Fig. 1b.

**Reaction of Tetramethylenecyclobutane (I) with Tetracyanoethylene.**—A solution of 0.362 g. (2.8 mmoles) of tetracyanoethylene in 40 ml. of tetrahydrofuran was added to 100 ml. of ethanol containing less than 80 mg. of I. The resulting solution was sealed under nitrogen and stirred at 4° for 24 hr. Most of the solvent was removed at 30° under reduced pressure and the remaining 4–5 ml. of solution was chromatographed on acid-washed alumina. The product was easily eluted with benzene. Evaporation of solvent left 96 mg. of nearly colorless crystals of IX which reacts only slowly with oxygen at room temperature.

*Anal.* Calcd. for  $C_{14}H_2N_4$ : C, 72.40; H, 3.47; N, 24.13; mol. wt., 232. Found: C, 72.06; H, 3.11; N, 24.04; mol. wt., 252.

The ultraviolet spectrum possesses an absorption maximum in acetonitrile at 209  $m\mu$  ( $\epsilon$  26,200) with a shoulder at 247.5  $m\mu$  ( $\epsilon$  4,090). Significant infrared absorption bands are found at 3092(m), 2994(w), 2964(m), 2931(m), 2251(w), 1711(m), 1653(s), 1428(m-s) and 874(vs)  $cm^{-1}$  (KBr). The n.m.r. spectrum reproduced in Fig. 1c and determined in acetonitrile has peaks at  $\tau = 5.13, 5.24$  and 6.45 with integrated areas of 1:1:2, respectively.

**Reaction of Tetramethylenecyclobutane (I) with N-Phenylmaleimide.**—A solution of I in ethanol (80 ml.) prepared from 1.0 g. of *trans,trans,trans*-1,2,3,4-tetrabromomethylcyclobutane (Va) was allowed to stand with 0.40 g. of N-phenylmaleimide at 4° for 2 days. The ethanol was then removed under vacuum and the residue after dilution with 4 ml. of benzene was chromatographed on acid-washed alumina. Two reaction products were isolated in approximately equal amounts. One compound (18 mg.) was eluted with the first 50 ml. of benzene and was shown to be the dimer VIII by comparison of its n.m.r. and infrared spectra with those of the authentic material. Unreacted N-phenylmaleimide was eluted with a solution of benzene-chloroform (20:1). The second product, a 1:1 Diels-Alder adduct of tetramethylenecyclobutane with N-phenylmaleimide, was eluted with 5:1 benzene-chloroform. When the reaction was conducted at 25° only the Diels-Alder adduct was isolated. The ultraviolet spectrum of this colorless, crystalline adduct X possesses an absorption maximum at 212.5  $m\mu$  ( $\epsilon$  37,800) and a shoulder at 248  $m\mu$  ( $\epsilon$  6,840). The n.m.r. spectrum observed in deuteriochloroform shows resonance peaks at  $\tau = 2.62$  (5), 5.30 (2), 5.41 (2), 6.68 (4) and 7.27 (2). Significant bands in the infrared spectrum (chloroform) are located at 3095(w), 2915(w), 2850(w), 1780(m), 1710(vs), 1749(m), 1610(m-w), 1430(m) and 865(m-s)  $cm^{-1}$  in addition to the characteristic phenyl absorption. An elemental analysis was not obtained on this adduct because of the difficulties associated with purifying and handling such an extremely oxygen-sensitive material.

**Preparation of Dihydropotetramethylenecyclobutane (XII).**—3,4-Dichloro-1,2,3,4-tetramethylcyclobutene (XI, 1.00 g., 5.6 mmoles) was dissolved in 15 ml. of *t*-butyl alcohol containing 1.7 g. (15 mmoles) of potassium *t*-butoxide and stirred under a nitrogen atmosphere at room temperature for 48 hr. The volatile product was then isolated by codistillation at 40° (0.02 mm.) into a Dry Ice-acetone trap and purification was achieved by preparative scale g.l.p.c. procedures using a silicone GE SF-96 column. The product possesses ultraviolet absorption maxima (isooctane) at 213 and 249  $m\mu$ . Minimum extinction coefficients (10,500 for  $\lambda_{max}$  213  $m\mu$  and 3530 for  $\lambda_{max}$  249  $m\mu$ ) were determined by assuming quantitative conversion of a weighed sample of XI to dihydropotetramethylenecyclobutane. The infrared spectrum determined in carbon tetrachloride shows significant peaks at 3089(m), 2970 (m), 2940(m), 2918(m), 2852(m-w), 1693(w), 1643(m-s), 1604(m), 1432(m), 1319 (m) and 852(vs)  $cm^{-1}$ . The mass spectrum of XII exhibits a parent mass, as

expected, at  $m/e$  106, almost as intense as the base peak at  $m/e$  91 which corresponds to loss of a methyl group. *t*-Butyl alcohol solutions of XII were employed for subsequent reaction studies because of the tendency of the pure hydrocarbon to oxidize.

**Catalytic Reduction of Dihydropotetramethylenecyclobutane (XII).**—A *t*-butyl alcohol solution of XII was hydrogenated over palladium-on-charcoal catalyst at atmospheric pressure. The catalyst was then collected on a filter and the filtrate subsequently gas chromatographed on a silicone GE SF-96 preparative column. The infrared spectrum and g.l.p.c. retention time of the major product were shown to be identical to those obtained for an authentic sample of *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane. Small amounts of isomeric hydrocarbons were also detected but not further characterized.

**Reaction of Dihydropotetramethylenecyclobutane (XII) with Tetracyanoethylene.**—To a *t*-butyl alcohol solution estimated to contain at least 32 mg. of dihydropotetramethylenecyclobutane (XII) was added to 140 mg. (1.1 mmoles) of tetracyanoethylene in 20 ml. of tetrahydrofuran. Immediately after addition of the tetracyanoethylene a cherry-red color developed which gradually faded as the reaction progressed. Stirring at room temperature was continued for 12 hr. The volatile solvents were then removed under reduced pressure at 35° and the residual orange solid was chromatographed on acid-washed alumina. The initial benzene fractions afforded 105 mg. of colorless crystals of the 1:1 adduct XIII. The ultraviolet spectrum of XIII determined in acetonitrile has a maximum at 227  $m\mu$  ( $\epsilon$  12,300) and the infrared spectrum (KBr) possesses significant absorption bands at 3090(w), 3031(m), 2980(m), 2958(m), 2922(m), 1692(m), 1629(s), 1432(s), 882(s) and 871(s)  $cm^{-1}$ . The n.m.r. spectrum is displayed in Fig. 1f and is consistent with the assigned structure.

*Anal.* Calcd. for  $C_{14}H_{10}N_4$ : C, 71.77; H, 4.32; N, 23.91; mol. wt., 234. Found: C, 71.62; H, 4.45; N, 23.84; mol. wt., 233 (ebullioscopic).

**Acknowledgment.**—The authors are indebted to the U. S. Army Research Office (Durham) and the Research Corporation, New York, N. Y., for mutual support of this work. We also wish to thank Miss R. Herberich and A. H. Struck of the Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., R. Jones, Esso Research and Engineering Co., Linden, N. J., as well as E. Schingh and H. Hoberecht of the Olin-Matheson Research Laboratories, New Haven, Conn., for mass spectral data. We also wish to thank N. F. Chamberlain and the n.m.r. group of the Humble Oil and Refining Co., Baytown, Tex., for the determination of certain n.m.r. spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

## The Mechanism of the Base-Initiated Dehydrohalogenation and Rearrangement of 1,1-Diaryl-2-bromoethylenes in *t*-Butyl Alcohol<sup>1</sup>

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RECEIVED DECEMBER 10, 1962

The reactions of the *cis* and *trans* isomers of 1-*p*-chlorophenyl-1-phenyl-2-bromoethylene and 1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene with a large excess of potassium *t*-butoxide in *t*-butyl alcohol at 95.6°, 109.1° and 119.2° have been studied. The ultraviolet spectra of the resulting diarylacetylenes (and reactants, where necessary) were used to follow the rates. It was found that the *trans* substituents had only small effects on the reaction rates (at 95.6°, methoxy accelerated the rate by a factor of *ca.* 2.5 relative to its *cis* isomer, whereas the chlorine slows the rate to *ca.* 0.4 times the rate of its *cis* isomer) but caused rather large effects on the activation parameters. Furthermore, it was found that no bromostilbenes accumulate during the reaction of the unsubstituted 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide. From these observations and the similarity of the effect of the groups on activation parameters to such reactions as the Beckmann rearrangement and the rearrangement of triarylmethyl azides it has been suggested that the best representation for the mechanism of the rearrangement portion of this reaction is the migration of the aryl group to a transition state involving an electron-deficient phenyl ring with concomitant loss of the halide ion.

The base-induced elimination of hydrogen halides from 1-halo-2,2-diphenylethylenes (the F.B.W. rearrangement) was first observed by Fritsch,<sup>3</sup> Buttenberg<sup>4</sup> and Wiechell.<sup>5</sup> Since the original investigations,

several studies have been made which have rather explicitly established certain aspects of the mechanism of this reaction. Thus, employing a combination of kinetics and deuterium isotope effects, Pritchard and Bothner-By<sup>6</sup> have shown that formation of diphenylacetylene from the reaction of 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol

(1) Based upon a thesis submitted by Ralph Damico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Texaco Research Fellow, 1960-1961.

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