

syringe inserted into the solution *via* the side arm of the cell. The samples were quenched to room temperature and aliquots were diluted to the desired volumes. No further reaction was noted in any of these cooled and diluted samples.

Ultraviolet spectra of the diluted solutions of anthracene from 6500 to 3000 Å. were recorded in either of two separate spectrophotometers. For solutions between 1.5×10^{-5} and 20×10^{-5} M a Beckman constant ratio instrument was used and for solutions below 2×10^{-5} M a Cary 14 spectrophotometer equipped with 5-cm. cell was used. The extinction coefficients were 6.0×10^3 and 7.2×10^3 on the two instruments, respectively, and accordingly, separate calibrations were made for each instrument. Beer's law was obeyed at 3790 Å. for all concentrations used on

both instruments and at this wave length no interfering absorptions from other reactants or products were observed.

The ultraviolet spectra for the other aromatics were measured on the Cary instrument. Beer's law was obeyed at all concentrations for α -benzoanthracene at 3600 Å. ($\epsilon 5.4 \times 10^3$) and for tetracene at 4760 Å. ($\epsilon 7.7 \times 10^3$), and no interfering absorptions were observed.

Acknowledgment.—The author acknowledges the helpful discussion in the course of the work and advice in the preparation of the manuscript rendered by Dr. C. H. Ruof.

[CONTRIBUTION NO. 3006 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

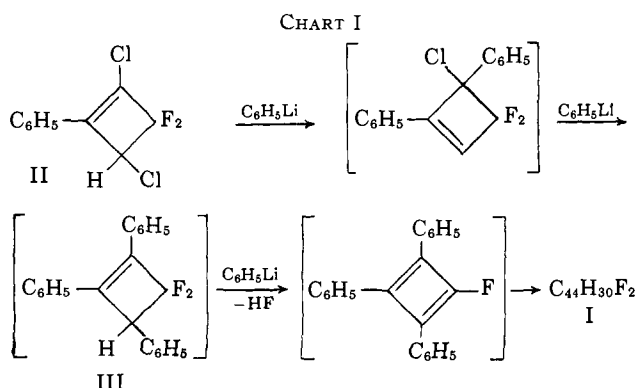
Small-Ring Compounds. XXXX. The Structure and Properties of a Dimer of Triphenylfluorocyclobutadiene¹

BY KUPPUSWAMY NAGARAJAN, MARJORIE C. CASERIO, AND JOHN D. ROBERTS

RECEIVED AUGUST 26, 1963

The chemistry of the previously described substance, $C_{44}H_{30}F_2$, from the reaction of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene and phenyllithium is described. The physical and chemical data presented are best interpreted in terms of an *anti*-tricyclo[4.2.0.0^{2,5}]octadiene structure for the substance which could arise by dimerization of triphenylfluorocyclobutadiene. The recent X-ray diffraction study of the substance by Hughes and Fritchie has confirmed the proposed structure.

During a recent study in this laboratory of nucleophilic displacement reactions of some halophenylcyclobutenes,² a substance was isolated of composition $C_{44}H_{30}F_2$ (I) from the reaction of phenyllithium with 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (II). We suggested that this substance could well be a dimer of triphenylfluorocyclobutadiene formed by the route outlined in Chart I. This route presumes attack of phenyllithium at the vinyl position of II in an $SN2'$ -type of displacement reaction to give a product which is rapidly attacked further by phenyllithium in a similar $SN2'$ reaction to give the triphenylcyclobutene derivative III; elimination of hydrogen fluoride from III would lead to triphenylfluorocyclobutadiene which could then dimerize to give I.

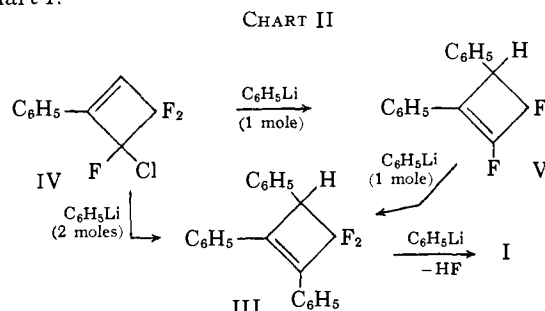


We have subsequently investigated in further detail the pathway by which the dimer I is formed, and the results of this work are described in this paper together with some of the interesting and unusual properties of the dimer.

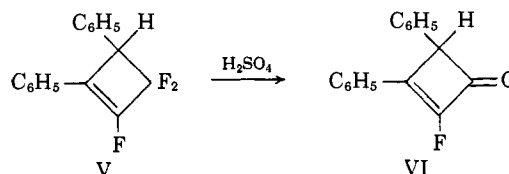
Formation of the dimer by the route given in Chart I involves, as the key intermediate, formation of 1,1-difluoro-2,3,4-triphenylcyclobutene (III). Evidence in support of the formation of III was obtained by the isolation of III from the reactions of phenyllithium with various other halophenylcyclobutenes, some of which

were prepared previously,³ and the demonstration that III does indeed react with phenyllithium to give the dimer I.

Starting with 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (IV), it was found possible to prepare the dimer I by reaction of IV with a 3–4 M excess of phenyllithium. The route by which this reaction could take place is given in Chart II and is closely similar to that of Chart I.



A significant experiment is the reaction of IV with only one molar equivalent of phenyllithium which gave a compound (m.p. 65–67°) that has been assigned structure V on the basis of its ultraviolet, infrared, and nuclear magnetic resonance spectra and the fact that it could be hydrolyzed with sulfuric acid to a ketone identified as having structure VI.



Treatment of V with a further molar equivalent of phenyllithium resulted in the displacement of the vinyl fluorine of V to give a compound identified as the difluorotriphenylcyclobutene III on the basis of spectral evidence and hydrolysis to a ketone identified as VII. Like other cyclobutenones,⁴ neither VI nor VII

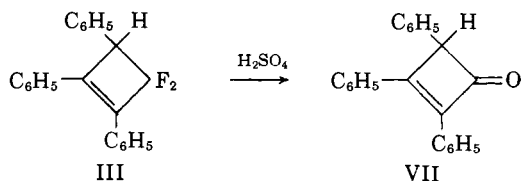
(1) Supported in part by the National Science Foundation.

(2) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

(3) (a) J. D. Roberts, G. B. Kline, and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953); (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

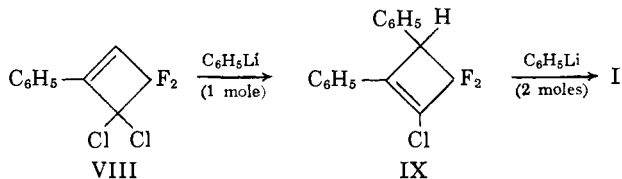
(4) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956).

appeared to enolyze to a hydroxycyclobutadiene derivative.



The key step in the proposed formation of I by Charts I and II is the reaction of III with phenyllithium. When this reaction was carried out with an authentic sample of III, the dimer I was indeed obtained, thus substantiating the proposed routes of Charts I and II.

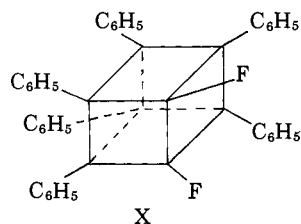
Dimer I could also be obtained from phenyllithium and 1,1-difluoro-2-chloro-3,4-diphenylcyclobutene (IX), which in turn was obtained from phenyllithium and 1,1-difluoro-2,2-dichloro-3-phenylcyclobutene (VIII).²



Several attempts were made to convert III to I with basic reagents other than phenyllithium, such as triethylamine, sodium methoxide, sodamide, and phenylmagnesium bromide, but without success. Also unsuccessful was an attempt to trap the intermediate triphenylfluorocyclobutadiene formed from III and phenyllithium by conducting the reaction in the presence of furan. A small yield of dimer was isolated as well as some starting material and uncharacterizable yellow gum.

Numerous experiments designed to improve the yield of I over that reported previously² (17%) were generally unsuccessful. Changes in the temperature of the reaction, alteration in the mole ratio of the reactants, or the order of addition did not give significantly better results, although the product was most easily purified when a solution of phenyllithium in ether was added to II. In addition to I, a small yield (1–2%) of a second compound was consistently obtained as white fluffy needles of m.p. 273°. A completely satisfactory elemental analysis for this compound was not obtained since it retained traces of solvent on recrystallization from methylene chloride; no further work was done to establish its structure.

The dimer I can be obtained as beautifully formed colorless crystals when recrystallized from a mixture of chloroform and ethanol. It turns yellow around 180° and melts with decomposition at 200°. The resistance of the compound to (a) oxidation with neutral or basic permanganate, (b) catalytic hydrogenation, and (c) addition of bromine in carbon tetrachloride, together with the absence of double bond absorption in the infrared, led to speculation that it might be a derivative of "cubane," such as X.⁵ However, this possibility



(5) Until recently, compounds with the "cubane" structure were unknown. However, the formation of octaphenylcubane by dimerization of tetraphenylcyclobutadiene has been reported: H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962), and references cited therein.

for the structure of I was ruled out on the basis of Raman and ultraviolet spectral evidence. The Raman spectrum⁶ of I showed very strong double bond absorption at 1645 cm.⁻¹, which indicates that the absence of the corresponding band in the infrared is due to symmetrical substitution of the double bond(s). This

definitely eliminates the chromophore C₆H₅C=C--F. Furthermore, the stretching frequency of the double bond(s) is very close to the strong 1642 cm.⁻¹ band observed in the Raman spectrum⁵ of III, and suggests the

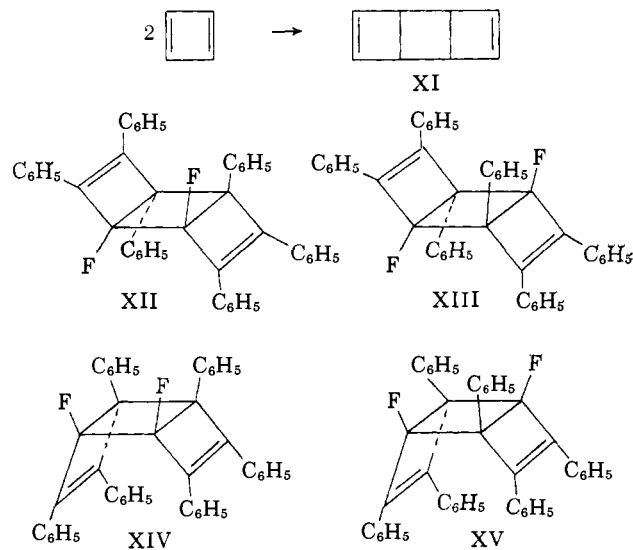
presence in I of the C₆H₅C=CC₆H₅ chromophore in a four-membered ring.

The ultraviolet spectrum of I has λ_{max} 288 mμ (ε_{max} 28,200) and λ_{max} 227 mμ (ε_{max} 53,100) while that of III has λ_{max} 294 mμ (ε_{max} 17,000) and λ_{max} 220 mμ (ε_{max} 28,900). The similarity in these spectra and that of *cis*-stilbene⁷ (λ_{max} 283 mμ, ε_{max} 12,300, and λ_{max} 222 mμ, ε_{max} 25,000) is further evidence for a *cis*-stilbene chromophore. In addition, the higher intensity of the absorption maxima of I suggests that two such chromophores are present.

The proton n.m.r. spectrum of I showed only resonance due to phenyl hydrogens while the fluorine spectrum had only a single peak, indicating the fluorines to be magnetically equivalent.

Attempts to degrade the dimer by chemical means were unsuccessful. The material added two moles of osmium tetroxide and reacted with two moles of ozone, but the products resisted satisfactory characterization. However, the results do indicate the presence of two double bonds.

If the "usual" mode of cyclobutadiene dimerization to a tricyclooctadiene structure XI^{8,9} occurred in the formation of I, then there are four structures possible for I as the result of *cis* addition with the double bonds having phenyl substituents. For these, XII–XV,



we can calculate that the dipole moments should be approximately 1.56 (XII), 0 (XIII), 3.5 (XIV), and 3.1 D. (XV) assuming a value of 1.92 D. for the

(6) Obtained through the courtesy of Dr. D. G. Rae, California Research Corporation.

(7) J. F. Codington and E. Mosetti, *J. Org. Chem.*, **17**, 1027 (1952).

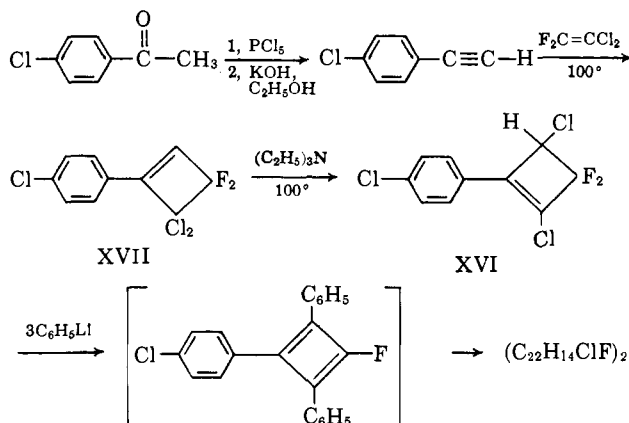
(8) (a) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957); *Chem. Ind. (London)*, 257 (1959); (b) M. Avram, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959); (c) M. Avram, Gh. Mateescu, I. G. Dinulescu, E. Marica, and C. D. Nenitzescu, *Tetrahedron Letters*, 21 (1961).

(9) (a) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957); (b) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); (c) R. Criegee, G. Schröder, G. Maier, and H. G. Fischer, *Chem. Ber.*, **93**, 1553 (1960).

dipole moment of the C-F bond.¹⁰ The measured value of the dipole moment of the dimer in benzene solution was 2.15 ± 0.08 D,¹¹ which agrees best with the structure XII. We therefore consider that the dimer is best described by structure XII on the basis of the physical and chemical data presented thus far.

At this point in our work, Dr. E. W. Hughes and Dr. C. J. Fritchie undertook an X-ray investigation of the dimer I.¹² To aid this investigation, it was decided to prepare the corresponding dimer $(C_{22}H_{14}ClF)_2$ derived from the reaction of phenyllithium with 1,1-difluoro-2,4-dichloro-3-(*p*-chlorophenyl)-cyclobutene (XVI)—the purpose being that a dimer of structure analogous to I but with two *p*-chlorophenyl substituents per molecule should aid the structure determination by X-ray crystallography by virtue of the presence of the relatively heavy chlorine atoms. The route followed for the synthesis of $(C_{22}H_{14}ClF)_2$ is given in Chart III; there was obtained a nicely crystalline compound of m.p. 194–196° dec. with closely similar spectral and chemical properties to I (see Experimental). However, the compound was not required for the X-ray investigation since, despite the extraordinary complexity of the structural problem of the dimer I, Hughes and Fritchie¹² were able to locate the positions of all the atoms in space and prove that structure XII is indeed the correct structure for the dimer I. Furthermore, recalculation of the dipole moment of I (XII) on the basis of the correct geometry determined by Hughes and Fritchie gave a value of 2.22 D., in close agreement with the experimental value of 2.15 ± 0.08 D.

CHART III



Formation of triphenylfluorocyclobutadiene and its subsequent dimerization to give XII is not surprising in the light of recent work from several laboratories^{5,8,9,13,14} on the behavior of cyclobutadiene itself and several derivatives. Although at one time it was thought that if cyclobutadiene were not actually a stable system, it would simply fragment to two molecules of acetylene, it now appears clear that the usual mode of self destruction of cyclobutadiene or its derivatives is by dimerization at low temperatures and possibly by ring opening at high temperatures. A possible exception has been noted for a cyclohexenylcyclobutadiene derivative which apparently isomerizes to a tetrahydronaphthalene.¹⁵

(10) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 273.

(11) We are indebted to Prof. R. M. Badger for his help with this determination.

(12) C. J. Fritchie, Jr., and E. W. Hughes, *J. Am. Chem. Soc.*, **84**, 2257 (1962).

(13) (a) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957); (b) M. P. Cava and J. F. Stucker, *ibid.*, **79**, 1706 (1957).

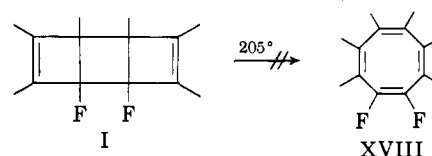
(14) E. H. White and H. C. Dunathan, Abstracts, 138th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 41P.

The dimerization of cyclobutadiene and its derivatives is theoretically likely on the basis of the simple molecular orbital treatment, which suggests that such substances should normally exist in triplet states with unpaired electrons.¹⁶ Furthermore, the dimerization has a parallel in the facile dimerization of cyclopentadiene since cyclopentadiene might be fairly regarded as a "homocyclobutadiene."

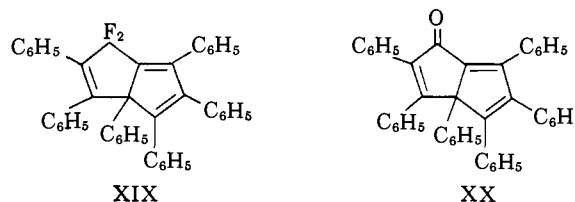
That a "head-to-head" dimer is formed has strong analogy in many other cycloaddition reactions which lead to cyclobutane or cyclobutene rings.¹⁷

The dimer I undergoes a thermal decomposition and rearrangement in different solvents to give a number of high-melting substances. Most of these have not been investigated in detail. Perhaps the most interesting of these reactions occurs when the material is kept above its decomposition point for 1–2 min. The product obtained in 85% yield is a yellow crystalline solid, m.p. 219–220° dec., which is isomeric with the starting material. This isomer is most reasonably formulated as the cyclooctatetraene derivative XVIII, but this structure is completely ruled out by the fluorine n.m.r. spectrum which shows that the two fluorines are magnetically nonequivalent. Furthermore, they must be located on the *same* carbon atom since the fluorine-fluorine spin-coupling constant has the value of 250

c.p.s., which is characteristic of an F-C-F arrangement.



Hydrolysis of the isomeric dimer, m.p. 220°, with sulfuric acid gave an orange ketone, m.p. 166–167.5°. The infrared spectrum of this compound shows a strong carbonyl absorption at 1710 cm^{-1} ; this suggests that the ketone might be a cyclopentenone, and the possibility that the yellow dimer and its corresponding ketone have structures XIX and XX, respectively, is being investigated.



On heating I in decalin solution for several minutes, hydrogen fluoride was evolved. The product recovered from the solution was a white crystalline solid of m.p. 337–338° which had a composition corresponding to the formula $C_{44}H_{29}F$. This material was not further investigated.

Experimental

Preparation of anti-1,2-Difluoro-3,4,5,6,7,8-hexaphenyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (I) from 1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene (IV).—To a stirred solution of 21.9 g. (0.1 mole) of IV in 100 ml. of ether was added 440 ml. (0.33 mole) of 0.76 *M* solution of phenyllithium in ether during 1 hr. The reaction was carried out at 0° in a nitrogen atmosphere. At the end of the addition, the red-violet reaction mixture was stirred

(15) C. M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 871 (1961).

(16) Cf. J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, **74**, 4579 (1952), and J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, Chapter 5, for references and discussion.

(17) J. D. Roberts and C. M. Sharts in A. C. Cope, Ed., "Organic Reactions," Vol. XII, John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 1.

for a further 2 hr. at 0°, then poured over a slush of ice and dilute hydrochloric acid. The products were extracted with ether, then chromatographed over acid-washed alumina in hexane. Elution with hexane-ether mixtures gave two colorless crystalline products which were separated by fractional crystallization from methylene chloride. The more soluble compound, I, (4.41 g.) had m.p. 200° dec. and λ_{\max} 227 m μ , ϵ_{\max} 53,100; λ_{\max} 288 m μ , ϵ_{\max} 28,200.

Anal. Calcd. for $C_{44}H_{30}F_2$: C, 88.56; H, 5.07; F, 6.37; mol. wt., 596. Found: C, 88.38; H, 5.15; F, 6.67; mol. wt. (isothermal distillation¹⁸), 570, 594.

The less soluble product (1.07 g.) had m.p. 273°, and λ_{\max} 231 m μ , $E_{1\%}^{1\text{cm}}$ 627; λ_{\max} 277 m μ , $E_{1\%}^{1\text{cm}}$ 817. Its fluorine n.m.r. spectrum had a single peak only.

Anal. Found: C, 90.70; H, 5.24; F, 3.28; mol. wt.,¹⁸ 635, 608.

Compound I was obtained similarly from the reaction of II, III, V, or IX with excess phenyllithium.

Thermal Isomerization of Dimer I.—Heating 0.10 g. of I at 210–215° for 75 sec. gave a red melt which, on cooling and washing with hexane, afforded 0.085 g. of a yellow crystalline powder. Recrystallization from acetone gave bright yellow crystals, m.p. 219–220° dec., λ_{\max} 250 m μ , ϵ_{\max} 28,600; λ_{\max} 373 m μ , ϵ_{\max} 13,570.

Anal. Calcd. for $C_{44}H_{30}F_2$: C, 88.56; H, 5.07; F, 6.37; mol. wt., 596. Found: C, 88.31; H, 5.22; F, 6.90; mol. wt. (isothermal distillation¹⁸), 590.

Hydrolysis of 0.050 g. of this yellow isomer of I with 0.1 ml. of concentrated sulfuric acid at 100° resulted in the evolution of hydrogen fluoride and the formation of an orange ketone, m.p. 166–167.5°. It is probably a hindered ketone since no 2,4-dinitrophenylhydrazone derivative could be prepared.

Anal. Calcd. for $C_{44}H_{30}C$: C, 91.96; H, 5.26; O, 2.78; mol. wt., 574. Found: C, 91.68; H, 5.55; O, 3.37; mol. wt. (isothermal distillation¹⁸), 563, 581.

A solution of 0.1 g. of I in 1 ml. of boiling decalin turned deep red within 2 min. with evolution of hydrogen fluoride. After 15 min. at reflux, the color lightened and no further hydrogen fluoride was evolved. The addition of pentane to the cool solution caused the precipitation of 20 mg. of white needles, m.p. 337–338° after recrystallization from a mixture of chloroform and acetone. Its ultraviolet spectrum had λ_{\max} 273 m μ , $E_{1\%}^{1\text{cm}}$ 978. In subsequent experiments, variable yields of this and the yellow substance $C_{44}H_{30}F_2$, m.p. 220°, were obtained.

Anal. Calcd. for $C_{44}H_{29}F$: C, 91.64; H, 5.07; F, 3.29; mol. wt., 577. Found: C, 91.27; H, 5.25; F, 3.71; mol. wt. (isothermal distillation¹⁸), 555.

1,1,2-Trifluoro-3,4-diphenyl-2-cyclobutene (V).—To a stirred solution of 10.9 g. (0.05 mole) of IV in 50 ml. of ether at 0° under nitrogen was added 0.06 mole of phenyllithium in 100 ml. of ether during 30 min. After a further 1.5 hr., the mixture was acidified and the product recovered from the ether solution. There was obtained 6.39 g. (73%) of slightly impure material, m.p. 65–67°, which is formulated as V. The compound had a strong absorption in the infrared at 1710 cm^{-1} characteristic of the grouping

$C_6H_5-C=C-F^{15}$; the ultraviolet spectrum of V in ethanol had λ_{\max} 252 m μ , ϵ_{\max} 20,000; the fluorine n.m.r. spectrum at 56.4 Mc.p.s. showed two doublets each with $J_{FF} = 203$ c.p.s., due to spin-coupling of the *gem*-fluorine substituents. Each line was further split due to spin-coupling with the vinyl fluorine and the allylic hydrogen. A resonance due to the vinyl fluorine was also observed as a complex of closely spaced lines, again due to spin-coupling with the allylic hydrogen and the *gem*-fluorine substituents.

Anal. Calcd. for $C_{16}H_{11}F_3$: C, 73.81; H, 4.26; F, 21.93. Found: C, 74.05; H, 4.53.

Sulfuric acid hydrolysis of V gave the ketone VI which had m.p. 83–84° after two recrystallizations from hexane.

The 2,4-dinitrophenylhydrazone of VI had m.p. 212° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{22}H_{15}FN_4O_4$: C, 63.16; H, 3.61; N, 13.39. Found: C, 63.45; H, 3.87; N, 13.22.

1,1-Difluoro-2,3,4-triphenylcyclobutene (III).—The reaction of IV with phenyllithium was repeated as described above for the preparation of V except that the mole ratio of phenyllithium to IV was increased to 2:1. The major product was III (38%), a colorless crystalline compound of m.p. 85–86° after recrystallization from pentane.

Anal. Calcd. for $C_{22}H_{16}F_2$: C, 83.00; H, 5.07; F, 11.94. Found: C, 82.83; H, 5.22; F, 12.53.

Compound III was assigned the structure 1,1-difluoro-2,3,4-triphenylcyclobutene on the basis of its ultraviolet spectrum which had λ_{\max} 294 m μ , ϵ_{\max} 17,000; λ_{\max} 220 m μ , ϵ_{\max} 28,900;

its infrared spectrum had no band at 1710 cm^{-1} characteristic of the grouping $C_6H_5-C=C-F^{15}$ and its fluorine n.m.r. spectrum showed a pair of doublets with $J_{FF} = 200$ c.p.s. characteristic of the grouping $F-C-F$; one doublet was further

split by spin-coupling with the allylic hydrogen, $J_{HF} = 6$ c.p.s. The Raman spectrum of III had a strong double bond stretch band at 1642 cm^{-1} .

Facile hydrolysis of III to the corresponding ketone VII, m.p. 112°, was effected with sulfuric acid or even with moist alumina.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44; O, 5.40. Found: C, 89.11; H, 5.55; O, 6.26.

The 2,4-dinitrophenylhydrazone of VII had m.p. 224.5°.

Anal. Calcd. for $C_{28}H_{20}N_4O_4$: C, 70.56; H, 4.23; N, 11.76. Found: C, 70.54; H, 4.29; N, 11.87.

The proton n.m.r. spectrum of the ketone showed resonances due to phenyl protons and a *single* peak for the allylic hydrogen.

***p*-Chlorophenylacetylene** was prepared from *p*-chloroacetophenone after the procedure described by Jacobs¹⁹ for the preparation of *p*-bromophenylacetylene. The product was obtained in 35% yield after two distillations at reduced pressure and had b.p. 77.0–77.5° (22–23 mm), m.p. 45.4–46.0° (lit.²⁰ m.p. 45.4–46.1°).

1,1-Difluoro-2,2-dichloro-3-(*p*-chlorophenyl)-cyclobutene (XVII).—A mixture of 14.9 g. (0.109 mole) of *p*-chlorophenylacetylene and 45 g. (0.338 mole) of difluorodichloroethylene was heated in a sealed heavy-wall Pyrex tube at 100° for 18.5 hr. The contents of the tube were then distilled at atmospheric pressure until the bath temperature rose to 120°, the distillate (3.25 g., b.p. 32–60°) being discarded. The residue was distilled at reduced pressure through a small Vigreux column to give 22.7 g. (77%) of an almost colorless oil, b.p. 99.0–99.5° (0.8–0.9 mm.), which crystallized on cooling, m.p. 49°. After four recrystallizations from hexane, the product (XVII) had m.p. 58.2–59.2°, λ_{\max} 266 m μ , ϵ_{\max} 23,700. The proton n.m.r. spectrum of XVII at 60 Mc.p.s. showed a quartet of lines for the aromatic protons and a triplet for the vinyl proton.

Anal. Calcd. for $C_{10}H_9F_2Cl_2$: C, 44.56; H, 1.87. Found: C, 44.48; H, 1.97.

1,1-Difluoro-2,4-dichloro-3-(*p*-chlorophenyl)-cyclobutene (XVI).—A mixture of 15.0 g. of XVII and 0.5 ml. of triethylamine was heated in a sealed Pyrex tube at 100° for 17 hr. The dark residue was then extracted with ether and dilute hydrochloric acid. The ether extract was dried over sodium sulfate, filtered, and evaporated. The residue was distilled under reduced pressure and gave 13.2 g. (91%) of a colorless oil, b.p. 94.0–95.8° (0.6–0.7 mm). Redistillation gave a middle fraction, b.p. 96.3–96.8° (0.7–0.8 mm), n_D^{20} 1.5720, λ_{\max} 273 m μ , ϵ_{\max} 26,000. The proton n.m.r. spectrum of this product (XVI) showed a quartet due to the aromatic protons and a doublet due to the allylic proton.

Anal. Calcd. for $C_{10}H_9F_2Cl_2$: C, 44.56; H, 1.87. Found: C, 44.39; H, 2.10.

Reaction of 1,1-Difluoro-2,4-dichloro-3-(*p*-chlorophenyl)-cyclobutene with Phenyllithium.—To a stirred solution of 7.35 g. (0.0273 mole) of XVI in 50 ml. of ether was added dropwise a threefold excess (0.082 mole) of phenyllithium in 55 ml. of ether. The reaction was carried out in a nitrogen atmosphere at –5 to 0°. When all the phenyllithium had been added (25 min.), the mixture was stirred for a further 80 min., then poured over crushed ice acidified with dilute hydrochloric acid, and filtered from a small amount of insoluble material. When dry, this white crystalline solid weighed 450 mg. and had m.p. 194.2–196.0° dec., discoloring at 180°; $\lambda_{\max} \sim 253$ m μ , $E_{1\%}^{1\text{cm}}$ 676.

Anal. Calcd. for $(C_{22}H_{14}FCl)_2$: C, 79.39; H, 4.24; mol. wt., 666. Found: C, 78.60; H, 4.26; mol. wt. (isothermal distillation), 688.

Although this material could well be a dimer of diphenyl-*p*-chlorophenylfluorocyclobutadiene, its ultraviolet spectrum indicates that it is not structurally related to dimer I. Therefore it was not investigated further.

The ether extract was dried over sodium sulfate, filtered, and evaporated. The residue was chromatographed over acid-washed alumina in hexane. The first fraction containing bromobenzene and biphenyl was discarded. Subsequent fractions eluted with 2 l. of hexane were combined and gave 1.16 g. of a yellow solid which, when recrystallized twice from chloroform and acetone and twice from methylene chloride and hexane, was obtained as well-formed colorless crystals, m.p. 200.5–202° dec., discoloring at 185°.

Anal. Calcd. for $(C_{22}H_{14}FCl)_2$: C, 79.39; H, 4.24; F, 5.71; Cl, 10.65; mol. wt., 666. Found: C, 78.96; H, 4.22; F, 4.90; Cl, 10.02; mol. wt. (isothermal distillation), 677.

(19) T. L. Jacobs, *Org. Reactions*, **5**, 50 (1949).

(20) T. H. Vaughn and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 1207 (1934).

The proton n.m.r. spectrum of this material in deuteriochloroform showed only a complex resonance due to aromatic protons. The fluorine n.m.r. spectrum had a single unresolved line at 165 p.p.m. from trichlorofluoromethane. The ultraviolet spectrum had λ_{\max} , 293 m μ , ϵ_{\max} 30,000; λ_{\max} 242 m μ , ϵ_{\max} 53,000; λ_{\max} 235 m μ , ϵ_{\max} 50,000. The resemblance between the ultraviolet

spectra of this material and I, *cis*-stilbene⁷ and *cis*-4-chlorostilbene²¹ strongly suggests that I and the *p*-chlorophenyl-substituted dimer are structurally related.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF YALE UNIVERSITY, NEW HAVEN, CONN., HAVERFORD COLLEGE, HAVERFORD, PA., AND THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.]

Dimers of 1,3-Diphenylcyclobutadiene from the Hofmann Elimination of 1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane Dimethiodide¹

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RECEIVED JULY 12, 1963

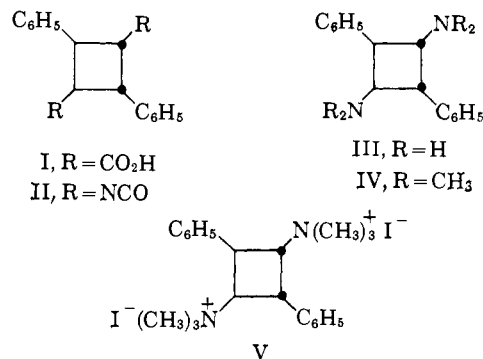
The reaction of 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane dimethiodide (V) with bases has been examined as part of a study of the chemistry of diphenylcyclobutadiene. The reaction with weak bases yields a cyclobutene derivative, 1,3-diphenyl-4-dimethylaminocyclobutene methiodide (VIa). The reaction with a strong base such as diethylamide ion yields, among other products, two tricyclooctadienes (X and XI), considered to be dimers of 1,3-diphenylcyclobutadiene. The latter compounds (X and XI) undergo an isomerization at room temperature to form 1,3,5,7-tetraphenylcyclooctatetraene (VIII) and 1,2,4,7-tetraphenylcyclooctatetraene (IX), respectively.

A renewal of interest in the chemistry of cyclobutadiene has occurred in recent years, presumably as one facet of the current interest in cyclic conjugated hydrocarbons. Only a few papers concerning cyclobutadiene appeared in the literature from 1905, the date of Willstätter's pioneering work on the subject,² to 1940. The synthesis of dibenzocyclobutadiene³ in 1941 refocused attention on this problem and led to the current intensive study of the cyclobutadienes.⁴

Although dibenzocyclobutadiene and its homologs are the only cyclobutadiene compounds that have been isolated to date, there is considerable evidence that simple nonring-fused cyclobutadienes may exist as transient reaction intermediates. This evidence includes the isolation of cyclobutadiene dimers,^{1,5} butadienes,⁶ Diels-Alder adducts⁷ and metal complexes⁸ of the cyclobutadienes, and the isolation of certain other reaction products.⁹ In this paper we present evidence, chiefly of the first kind, for the existence of diphenylcyclobutadiene as a reaction intermediate.

The reaction examined was the Hofmann elimination of 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane dimethiodide (V), a compound readily prepared from cinnamic acid.¹⁰ At the time, it was hoped that the phenyl groups might confer a certain degree of sta-

bility on the cyclobutadiene and also increase the rate of the elimination reaction. The stereochemistry of the diamine was such that both *trans* and *cis* elimination could be effected, and therefore, advantage could be taken of both the Hofmann elimination and the amine oxide pyrolysis reactions. It was hoped, furthermore, that the 1,3-arrangement of functional groups would avoid the formation of stable vinyl ammonium salts, a difficulty encountered with 1,2-disubstituted cyclobutanes.¹¹



The conversion of α -truxillic acid (I) into 1,3-diphenyl-2,4-diaminocyclobutane (III) by the Curtius reaction has been described in an earlier paper.¹⁰ Methylation of this amine by the Eschweiler-Clark method¹² yielded 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane (IV)¹³; the stereochemistry assigned (IV) follows from the method of synthesis¹⁰ and the n.m.r. spectrum, which showed a typical A₂B₂ multiplet. It was found, subsequently, that the hydrolysis step II \rightarrow III could be by-passed, and that good yields of the tetramethyldiamine IV could be obtained through treatment of the diisocyanate II directly with formaldehyde and formic acid.¹⁴ Quaternization of the

(11) E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *ibid.*, **64**, 2696 (1942); see also p. 2701.

(12) M. L. Moore, "Organic Reactions," Coll. Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 307.

(13) The bis-oxide of this compound was prepared and pyrolyzed; a complex mixture was obtained from which no pure olefinic material could be isolated. A possible side reaction in this case would be a rearrangement of the monoeliminated material to the corresponding O-alkylhydroxylamine [A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949)].

(14) Less efficient synthetic sequences involved reduction of II to the methyldiamine followed by the Eschweiler-Clark methylation to IV, on the one hand, and formation of the benzyl alcohol derivative of II followed by catalytic hydrogenation to give the diamine III, on the other.

(1) Presented, in part, before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958 (p. 41P of the abstracts). Taken in part from a thesis submitted by Harmon C. Dunathan to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree.

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(3) W. C. Lothrop, *J. Am. Chem. Soc.*, **63**, 1187 (1941).

(4) For reviews of the cyclobutadiene literature, see W. Baker and J. F. W. McComie, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter II; E. Vogel, *Angew. Chem.*, **72**, 4 (1960); and R. Criegee, *ibid.*, **74**, 703 (1962).

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(7) C. D. Nenitzescu, M. Avram, and D. Dinu, *Ber.*, **90**, 2541 (1957); C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961); R. C. Cookson and D. W. Jones, *ibid.*, 115 (1963).

(8) (a) R. Criegee and G. Schröder, *Angew. Chem.*, **71**, 70 (1959); (b) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (c) M. Avram, E. Marica, and C. D. Nenitzescu, *Ber.*, **92**, 1088 (1959).

(9) (a) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961); (b) C. M. Sharts and J. D. Roberts, *ibid.*, **83**, 871 (1961).

(10) E. H. White and H. C. Dunathan, *ibid.*, **78**, 6055 (1956).