JOC Article

Chemistry of 1-Fluoro-2,3,4-triphenylcyclobutadiene Dimers

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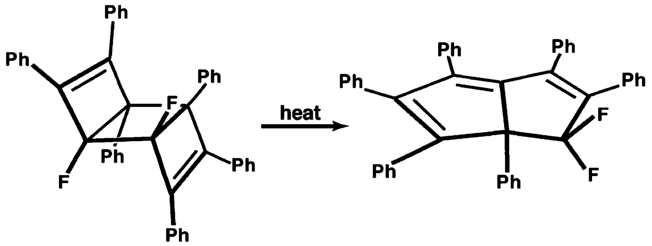
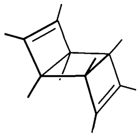
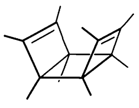


The reaction of 2,4-dichloro-1,1-difluoro-3-phenyl-2-cyclobutene **1** with excess phenyllithium and subsequent transformations of the products have been reinvestigated. The phenyllithium reaction appears to proceed through the intermediacy of a fluorotriphenylcyclobutadiene **2** to produce a well-characterized dimeric *trans*-hexaphenyldifluorotricyclooctadiene **3a**. Subsequent transformations of **3a** gave a pentaphenyldihydrodifluoropentalene **4**, which on acid hydrolysis formed a pentaphenyldihydropentalenone **5**. When **3a** was photolyzed in benzene, after purification, it afforded **6**, an isomer of **5**, probably by way of **7**, an isomer of **4**. Thermolysis of **3a** also provided, in low yield, a substance believed to be a pentaphenylfluorophenanthrene **8**. Along with isolation of **3a**, and probably arising from a different isomer of the **3** family, was a pentaphenylfluorophenanthrene **9**, which was suspected of being an isomer of **8**. Single-crystal X-ray studies were used to derive structures for **4**, **5**, **6**, and **9**. Formation of the unusual and intriguing transformation products has at least been rationalized.

Introduction

In the course of investigations 45 years ago of the reaction of phenyllithium with 2,4-dichloro-1,1-difluoro-3-phenyl-2-cyclobutene **1**, it was discovered that excess phenyllithium gave a mixture of products and, through at least partial intermediacy of fluorotriphenylcyclobutadiene **2**, formed a dimer **3a**, $C_{44}H_{30}F_2$, mp 200 °C (d) in about 17% yield.[1−3] Dimerizations of cyclobutadienes to 2,3,7,6-tricyclo$[0^{1,4}.0^{5,8}]$octadienes are well-known reactions, but in the case of **2**, there are a rather large number of possible structures. However, omitting enantiomers, assuming cis addition and also that cycloaddition occurs only to form dimers with double bonds substituted exclusively with phenyl groups, there are four possible different dimers, provided we consider both the “sofa” **10a** and “tub” **10b** forms.


10a (sofa)


10b (tub)

Originally,[3] without today’s more powerful methods of structural characterization, it was necessary to proceed in a stepwise manner. Thus, UV and Raman spectral data indicated only tetrasubstituted *cis*-stilbene-like double bonds. Proton NMR showed only phenyl proton chemical shifts, while fluorine NMR gave a single shift for the two fluorine atoms. These data allowed us to conclude that the dimer had the tricyclooctadiene framework with six phenyl groups and two fluorine atoms. Dipole moment determinations further narrowed the four structural possibilities (two sofa and two tub) uniquely to **3a**,[3]

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[§] California Institute of Technology.

(1) Kitahara, Y.; Caserio, M. C.; Scardiglia, F.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 3106−3111.

(2) Nagarajan, K.; Caserio, M. C.; Roberts, J. D. *Rev. Chimie* **1962**, *7*, 1109−1117.

(3) Nagarajan, K.; Caserio, M. C.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 449−453.

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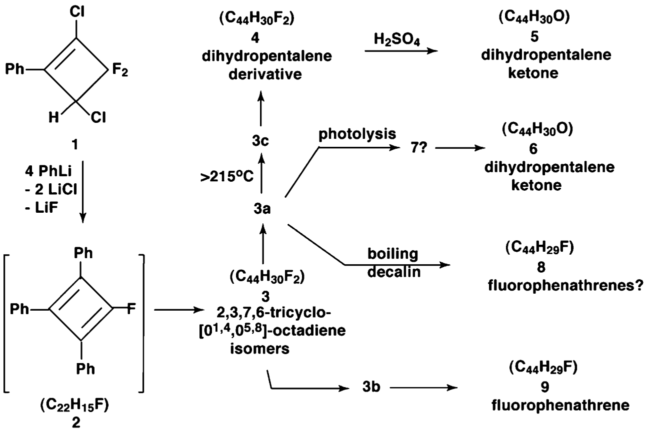
SCHEME 1. Reaction Synopsis



which was confirmed by a difficult (for that period) single-crystal X-ray study.[4] Efforts to prove the structure of **3a** by chemical degradation reactions were unsuccessful, but in the process of trying, several crystalline compounds were obtained, of which only two could even be assigned tentative structures, in our original work. Scheme 1 is a roadmap of the various reactions and the general character of their products. The continued availability of the samples and current interest in F, F interactions in crystals of fluoroaromatics,[5] prompted further investigation of these substances.

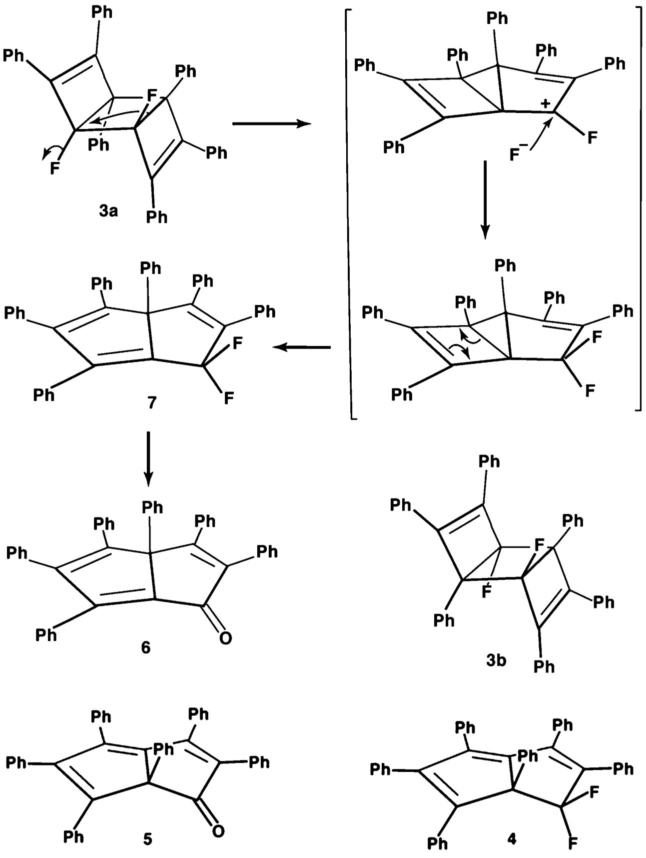
Results and Discussion

Our current studies of **3a** have confirmed the molecular formula, $C_{44}H_{30}F_2$, by its mass spectrum. The proton NMR spectrum in $CDCl_3$ at 300 MHz (vs 40 MHz in 1960) gave only signals in the aromatic region. Strikingly, **3a** showed two approximate doublets at 6.75 (4H) and 7.64 ppm (4H), which were not coupled to each other. The other 22 protons were seen as indistinct multiplets between 6.9 and 7.4 ppm. The doublets at 6.75 and 7.64 ppm were unexpected and could well involve the ortho protons of the phenyl groups adjacent to the fluorine atoms in **3a**. The ^{13}C NMR spectrum of **3a** at 75 MHz showed quaternary carbons at 99.2 ppm with $^{13}J_{1CF}$ values of 274 Hz and $^{13}J_{2CF}$ of 28 Hz. The saturated quaternary carbons carrying phenyl groups were at 69.38 ppm as triplets arising from coupling with the nearby F atoms.

When heated above its melting point, 210−215 °C, for 75 s, **3a** gave a red melt, which when triturated with hexane afforded an 85% yield of yellow crystalline **4**. Traces of an isomer of **4**, thought to be **7**, were detected in this reaction. Compound **4**, $C_{44}H_{30}F_2$, was isomeric with **3a**, but with two magnetically nonequivalent geminal fluorine atoms ($^1J_{FF} = 250$ Hz) in its NMR spectrum. On hydrolysis with sulfuric acid, **4** afforded yellow **5**, $C_{44}H_{30}O$, with a ketonic C=O band in the IR at 1710 cm^{-1}. The ketone was apparently hindered at the carbonyl group because it did not form a 2,4-dinitrophenylhydrazone derivative.

A possible mechanism for conversion of **3a** to a *gem*-difluoro compound would involve ionization of one of the equivalent fluorines, a conventional cationic cyclobutyl-to-cyclopropylmethyl rearrangement, followed by fluoride ion return to afford a *gem*-difluoride, which after hydrolysis would give the ketone **6** (see Scheme 2). Despite the plausibility of the mechanism, the product was not **6** but was shown quite surprisingly by single-crystal X-ray diffraction to be **5** (see Figure 1). To make matters more interesting, **5** cannot be formed by a route similar to Scheme 2, either from **3a** or **3a**'s very reasonably formed isomer **3b**, by as simple a mechanism as that proposed for **3a** to **6**. However, a somewhat more complicated mechanism via **3c** and **4** leading to **5** is shown in Scheme 3, which requires that **3c** be formed by heating **3a**.

SCHEME 2. Possible Isomerization Processes of 3a



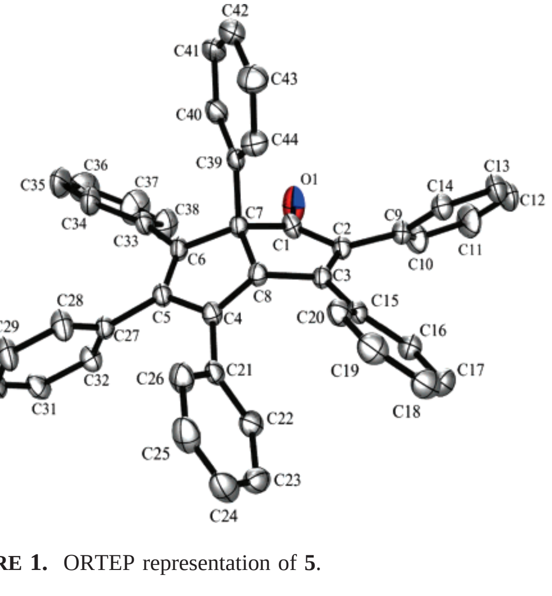


FIGURE 1. ORTEP representation of **5**.

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[4] Fritchie, C. J.; Hughes, E. W. *J. Am. Chem. Soc.* **1962**, *84*, 2257−2258.

[5] Choudhury, A. R.; Nagarajan, K; Guru Row, T. N. *Cryst. Eng.* **2004**, *6*, 43.

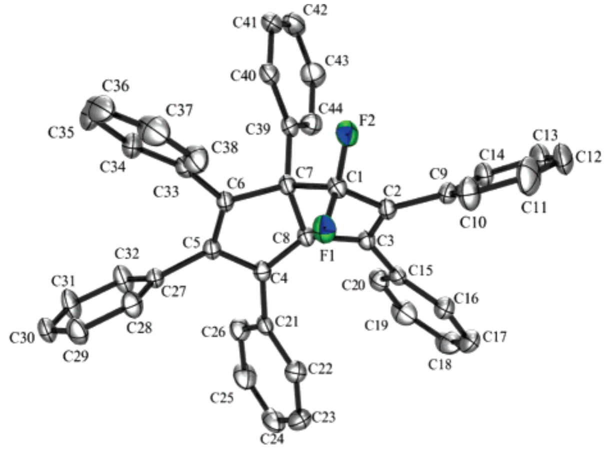


FIGURE 2. ORTEP representation of **4**.

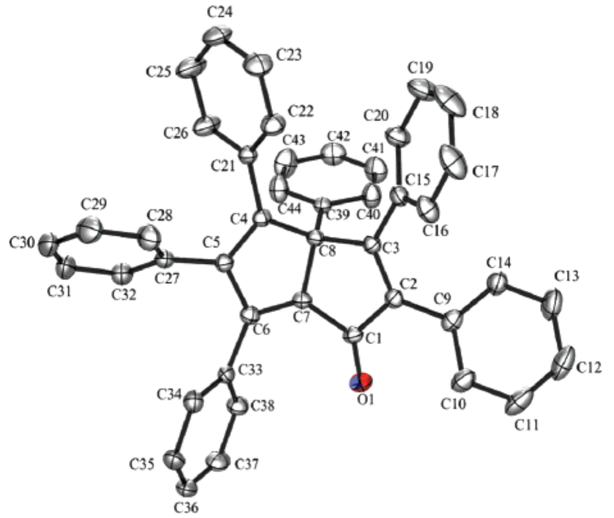


FIGURE 3. ORTEP representation of ketone **6**.

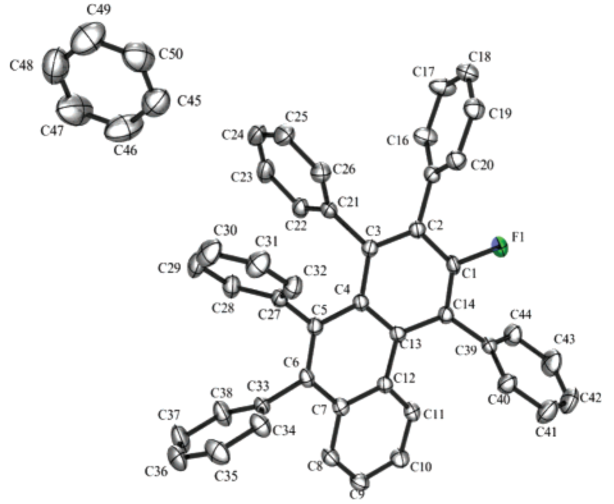
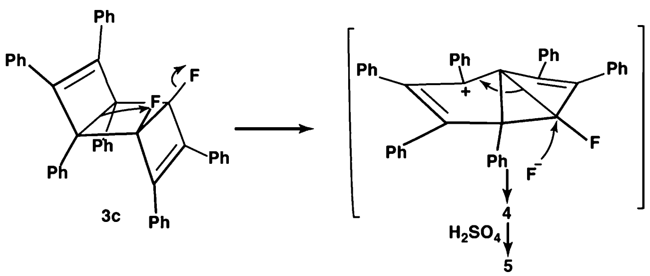


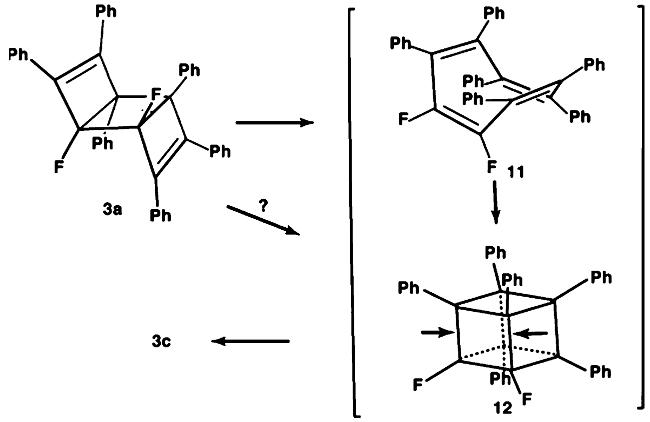
FIGURE 4. ORTEP representation of **9**.

One reasonable way of having that happen would be to have **3a** open to the cyclooctatetraene **11** and then isomerize to **3c** by way of the corresponding cubane **12**, or else **3a** going directly to **12** and thence to **3c**, both as shown in Scheme 4. Octaphenylcubane has been reported via the intermediacy of octaphenylcyclooctatetraene or octaphenylcyclo$[0^{1,4}]$octadiene.[6] That **4** is formed preferentially by heating **3a** is likely to be the result of strong steric interactions between the phenyl groups expected for **7** compared to **4**, as is evident in Figure 2 and seen quite dramatically by comparing the crystal structures of **5** (Figure 1) and **6** (Figure 3).

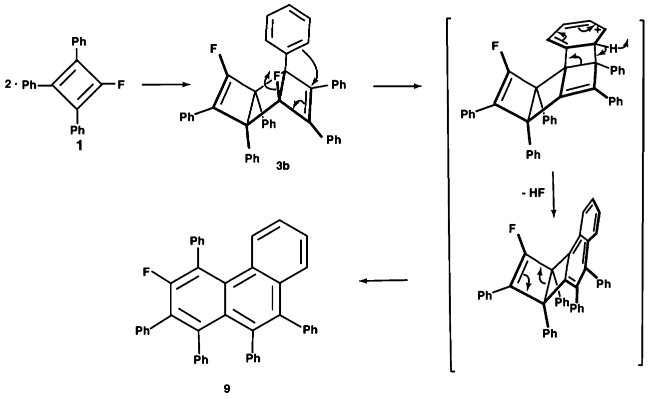
SCHEME 3. Possible Formation of 5 from 3c



SCHEME 4. Possible Route for Formation of 3c from 3a



SCHEME 5. Possible Isomerization Route from 3b to Phenanthrene Derivative 9



Oddly, photolysis of **3a** in benzene using a medium-pressure mercury lamp, followed by chromatography on alumina, afforded 15% of a yellow ketone of mp 199−199 °C, which by single-crystal X-ray diffraction turned out to be **6** (Figure 3), which may have been formed from the corresponding difluoride **7** by hydrolysis catalyzed by alumina in the chromatographic purification.

In the reaction of phenyllithium with **1**, a small yield (3.5%) of a second compound **9** was consistently obtained as white

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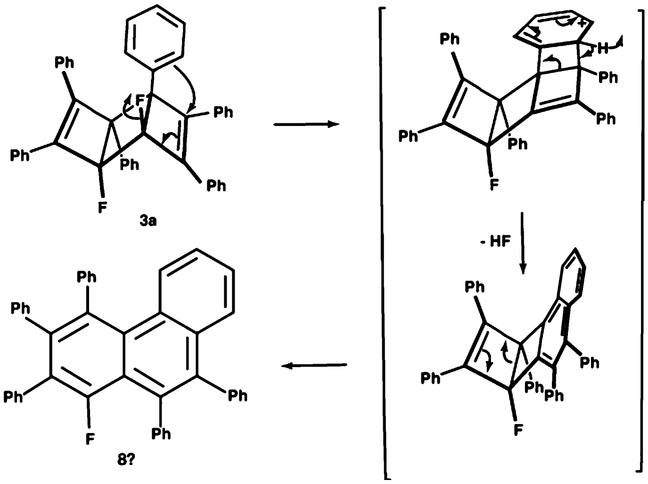
(6) Freedman, H. H.; Petersen, D. R. *J. Am. Chem. Soc.* **1962**, *84*, 2837−2838.

SCHEME 6. Possible Route from 3a to 8



fluffy needles, mp 273 °C. This compound had the molecular formula $C_{44}H_{29}F$, as shown by elemental analysis and molecular weight determined by isothermal distillation. Its ^{19}F NMR spectrum had a single broad peak, while its ^{13}C spectrum showed a quaternary carbon coupled to fluorine with a $^{13}J_{CF}$ of 244 Hz. The UV spectrum in cyclohexane had maxima at 210, 234, an 280 nm with a shoulder at 326 nm. These data were suggestive of an aromatic hydrocarbon, and this was confirmed by single-crystal X-ray diffraction to be **9** (see Scheme 5 and Figure 4) assumed to be formed through the intermediacy of a different dimer of **1**, designated as **3b**, which could lead to **9**, first by an ortho-electrophilic cyclization on a phenyl group, followed by bond reorganizations to form a phenanthrene derivative. This cyclization has a parallel in isomerization of a cyclohexenyl-cyclobutadiene to a tetrahydronaphthalene.[7]

When **3a** was heated in boiling decalin for 2 min, hydrogen fluoride was evolved and a 20% yield of a white substance **8** of mp 337−338 °C was obtained, along with larger amounts of **4** and **5**. The solid **8** was $C_{44}H_{29}F$ by mass spectrometry and thus an isomer of **9**. The resemblance was heightened by its UV spectrum in cyclohexane with absorption maxima at 210 and 276 nm with shoulders at 228 and 324 nm. Unfortunately, useful proton and carbon NMR spectra or suitable crystals for single crystals could not be obtained for single-crystal diffractions studies, although XRD indicated crystallinity. It is possible that the product is a mixture of isomers, but a principle component could be structure **8**, which would arise in a straightforward way from **3a** by Scheme 6, analogous to Scheme 5.

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Supporting Information Available: Details of the X-ray diffraction studies, packing diagrams, and CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Sharts, C. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 871−878.