after extraction with caustic and vacuum distillation at ~70 °C (0.1 mm), the crude product was recrystallized twice from methanol at -78 °C. The resulting sample was pure by packed column GC and by both ^1H and ^{13}C NMR. ^1H NMR (300 MHz): 3.90 (^1H), 1.95 (2 H), 1.75 (2 H), 1.1–1.6 ppm (6 H). ^{13}C NMR: 80.86 (C1), 30.53 (C2C4), 25.66 (C6), 23.77 (C3C5). DCHP can also be prepared by reaction of KO_2 with cyclohexyl toluenesulfonate.[33]

Laser Flash Photolysis Experiments. Flash experiments were performed essentially as described by Scaiano et al.[24,29] Transients were collected by means of a RCA Model 4840 photomultiplier operated at -900 V dc and terminated into 50 ohms at the input of a Tektronix Model 7912AD transient digitizer. A differential amplifier was used to allow expansion and offsetting of weak signals so that maximum digitial resolution was possible. A total of 1024 channels of data was collected at a scan rate of 5 ns/channel. Individual, single-shot transients were transferred to the DEC-MINC computer and subsequently averaged, analyzed, plotted, and transferred to a DECSYSTEM-10 computer for storing and further analysis.

Samples for flash photolysis were prepared from stock solutions by serial dilution into 1 cm by 1 cm fluorescence cells with graded seals. The samples were degassed with an argon purge for 20–30 min at 0 °C and sealed by means of serum stoppers. The concentration of DCHP was no higher than 10 v/v%, which gave an OD at 308 nm of 1.0.

Diphenylmethanol was triply sublimed and used promptly after purification. Chlorobenzene was used as received and gave equivalent results to freshly distilled material. 1,4-Cyclohexadiene was used as received. Other reagents were of the highest purity available and were generally distilled prior to use.

(33) Druliner, J. D. *Synth. Commun.* **1983**, *13*, 115.

New Routes to Hexafluorocyclopentadiene and Related Compounds[1]
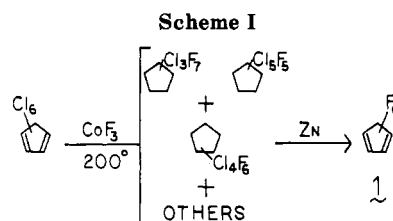
Richard R. Soelch, George W. Mauer, and David M. Lemal*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Hexafluorocyclopentadiene (1) has been synthesized in two steps from pentafluorophenol (2) by fluorination followed by flash vacuum pyrolysis of the resulting hexafluorocyclohexadienones 3 and 4. Similar pyrolysis of 6-chloropentafluorocyclohexadienone (13) gave an equilibrium mixture of 1- and 2-chloropentafluorocyclopentadiene (15 and 16), presumably via the 5-chloro isomer. Flash vacuum pyrolysis of tetrafluoro-*o*-benzoquinone (17) yielded tetrafluorocyclopentadienone (20). Hexafluorocyclopentadiene was also prepared via a ring-expansion route which entailed cycloaddition (accompanied by rearrangement) of bromotrifluoroethylene to tetrafluorocyclopropene followed by reductive debromofluorination.

As a versatile diene in the Diels–Alder reaction, hexafluorocyclopentadiene (1) is an important basic building block in organofluorine chemistry.[2] The compound was first synthesized by Banks, Haszeldine, and Walton in 1963,[3] and it has been prepared subsequently by a variety of methods.[4–6] With the exception of a modified version of the original synthesis,[2c,e] all of these routes give low yields. The Banks approach, shown in Scheme I, entails fluorination of hexachlorocyclopentadiene over cobaltic fluoride at 200 °C, fractionation of the product, and dechlorination with zinc of the tetrachloro fraction. Recycling of other fractions from the fluorination is required to obtained good yields (up to 42% overall). The apparatus required for the fluorination is a stirred-bed steel reactor which is available in very few laboratories. We were thus stimulated to seek a route to hexafluorocyclopentadiene which is simple, efficient, and capable of execution in an ordinary laboratory. Though there remains room for improvement, we have developed an attractive alternative to the Banks synthesis.

Whereas all previous approaches to hexafluorocyclopentadiene have proceeded from starting materials having five-membered rings, we began with pentafluorophenol. This compound is quite expensive, but it is easily prepared from the much cheaper hexafluorobenzene in yields exceeding 90%.[7] The key idea for this synthesis was suggested by work of DeJongh's group, who found that high-temperature flow pyrolysis of *o*-benzoquinone[8] and

Scheme I

(1) This paper is based on the Ph.D. Dissertations of R. R. Soelch (1984) and G. M. Mauer (1983), Dartmouth College.

(2) (a) Banks, R. E.; Haszeldine, R. N.; Prodgers, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 596–598. (b) Banks, R. E.; Birks, L. E.; Haszeldine, R. N. *J. Chem. Soc. C* **1970**, 201–203. (c) Banks, R. E.; Bridge, M.; Haszeldine, R. N. *Ibid.* **1970**, 48–49. (d) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N.; Orrell, K. G. *Ibid.* **1967**, 1608–1621. (e) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *Ibid.* **1966**, 2102–2106. (f) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* **1966**, 338–339. (g) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *Ibid.* **1965**, 41–42.

(3) Banks, R. E.; Haszeldine, R. N.; Walton, J. B. *J. Chem. Soc.* **1963**, 5581–5583.

(4) Moore, E. P. U.S. Patent 3 686 336, 1972; *Chem. Abstr.* **1973**, *78*, P3832u.

(5) Harris, J. F., Jr. U.S. Patent 3 449 304, 1969.

(6) Burdon, J.; Hodgins, T. M.; Perry, D. R. A.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1965**, 808–810.

(7) National Polychemicals, Inc. Br. Patent 887 691, 1962; *Chem. Abstr.* **1962**, *56*, 11788e.

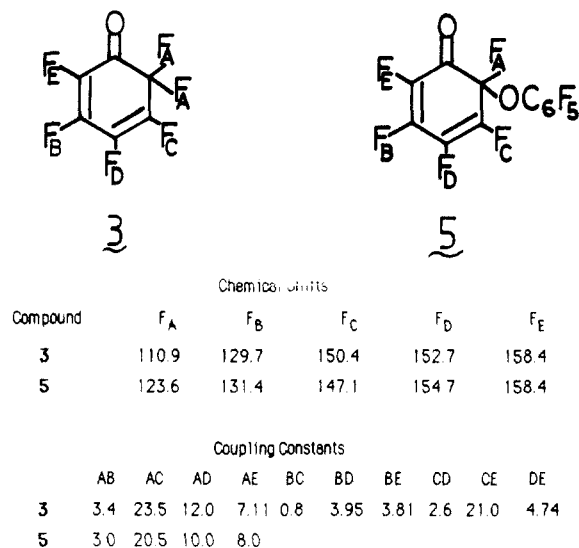(8) DeJongh, D. C.; Van Fossen, R. Y.; Bourgeois, C. F. *Tetrahedron Lett.* **1967**, 271–275.

Figure 1. A comparison of ^{19}F NMR data for two 2,4-cyclo-hexadienones.

Chemical Shifts

Compound	F_A	F_B	F_C	F_D	F_E
3	110.9	129.7	150.4	152.7	158.4
5	123.6	131.4	147.1	154.7	158.4

Coupling Constants

	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
3	3.4	23.5	12.0	7.11	0.8	3.95	3.81	2.6	21.0	4.74
5	3.0	20.5	10.0	8.0						

tetrachloro-*o*-benzoquinone[9] yields the dimers of the corresponding cyclopentadienones. Chapman and McIntosh
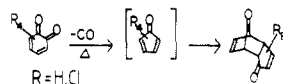
were able to obtain cyclopentadienone itself in matrix isolation by this method.[10]   It seemed likely, then, that 2,4-cyclohexadienones would also decarbonylate pyrolytically to give cyclopentadienes. Thus, we proposed to prepare hexafluorocyclopentadiene by fluorination of pentafluorophenol (2) followed by pyrolysis of the resulting hexafluoro-2,4-cyclohexadienone (3).
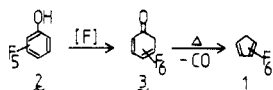

Results and Discussion

Fluorination of Pentafluorophenol. The desired 2,4-dienone had been made previously by two methods. Treatment of pentafluoroisopropoxyphenol with xenon difluoride gave this compound in 20% yield, together with a comparable amount of the 2,5-dienone 4.[11] Barlow, et al. prepared the 2,4-dienone in good yield by pyrolysis of hexafluorobenzene oxide.[12] The problem with the latter approach is that the oxide is formed slowly in very low yield in the photooxidation of hexafluorobenzene. We therefore explored new ways to fluorinate pentafluorophenol.

Initial efforts focused on trifluoromethyl hypofluorite,[13] which gave at room temperature reasonable yields of a mixture of the 2,4- and 2,5-dienones in a ratio of 4 or 5 to 1. Though even higher selectivity (10:1) could be achieved at lower temperatures, the reaction was inefficient under

these conditions. Infrared, mass spectral, and ^{19}F NMR
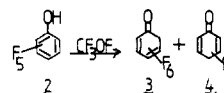
data on both compounds agreed with the literature values. A complete analysis of the complex but the first-order ^{19}F NMR spectrum of 3 was carried out with the help of decoupling experiments, and the spectrum was accurately simulated by computer. The chemical shift and coupling constant assignments are presented in Figure 1. The chemical shifts are very close (with the expected exception of that for F_A) to the analogous ones in dienone 5, which were assigned by Yakobson and co-workers.[14] Close similarities will also be noted between the coupling constants reported for dienone 5 (those for F_A) and the corresponding values for 3. The large value of J_{CE} (21 Hz) may seem surprising, but it agrees well with 1,4-F,F coupling constants reported for other 1,3-dienes, for example the largest $J_{1,4}$ in 1,1,4,4-tetrafluorobutadiene (23.2 Hz).[15]

Choice of conditions for the fluorination of 2 with trifluoromethyl hypofluorite must be made carefully. If unreacted phenol remains at the end of the reaction, it readily destroys the highly reactive 2,4-dienone by addition/elimination to give phenoxy dienone 6. Attempts to remove the acidic 2 from the product mixture by extraction with base simply accelerated the unwanted condensation. Similar results were obtained when the product was washed with cold water or treated with solid sodium bicarbonate to remove 2. Mixtures of 2 and 3 formed 6 even in the freezer over a period of several days. Formation of 6 was minimized by using excess fluorinating agent, but again care was required since trifluoromethyl hypofluorite transforms dienone 3 into tar in a process which appears to be catalytic if they are allowed to remain in contact for hours.
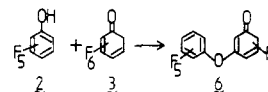
The position of substitution in 6 was indicated by the fact that the dienone portion of the ^{19}F NMR spectrum of 6 was almost identical with that of 3 save for the absence of F_B. As confirmation, Shteingarts and co-workers found that oxygen nucleophiles always displaced the analogous fluorine (at C-3) in 6-chloropentafluoro-2,4-cyclohexadienone.[16]

A further complication attended the fluorination of 2 with trifluoromethyl hypofluorite. The trifluoromethanol formed as a byproduct in the reaction undergoes an exothermic decomposition even at −20 °C to carbonyl fluoride and hydrogen fluoride.[17] Pentafluorophenol reacts with carbonyl fluoride to yield the fluoroformate 7 and carbonate 8.[18] This problem was solved by including an
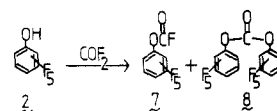
(9) DeJongh, D. C.; Brent, D. A.; Van Fossen, R. Y. *J. Org. Chem.* **1971**, *36*, 1469–1474.

(10) Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc., Chem. Commun.* **1971**, 770–771.

(11) Zupan, M.; Stavber, S. *J. Org. Chem.* **1981**, *46*, 300–302.

(12) Barlow, M. G.; Haszeldine, R. N.; Peck, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 158–159.

(13) Trifluoromethyl hypofluorite has been useful for the introduction of fluorine into benzene derivatives and carbonyl compounds. See, for example: (a) Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647–667; (b) Middleton, W. J; Bingham, E. M. *J. Am. Chem. Soc.* **1980**, *102*, 4846–4848.

(14) Kobrina, L. S.; Kovtonyuk, V. N.; Yakobson, G. G. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *13*, 1331–1335.

(15) Servis, K. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 1339–1344. These couplings result apparently from through-bond interactions (Newmark, R. A.; Apai, G. R.; Michael, R. O. *J. Magn. Reson.* **1969**, *1*, 418–431).

(16) Akhmetova, N. E.; Kostina, N. G.; Shteingarts, V. D. *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 1934–1944.

(17) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 322–323.

(18) Falardeau, J. R.; Desmarteau, D. D. *J. Fluorine Chem.* **1976**, *7*, 409–413.

Scheme II

I.P. = 10.9 eV   50%

I.P. = 10.0 eV   30%   30%

Scheme III
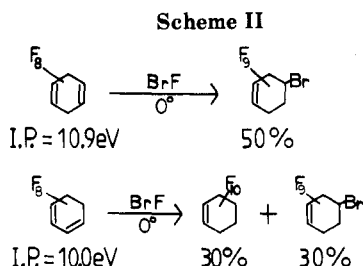
equivalent of water in the reaction mixture for each equivalent of trifluoromethyl hypofluorite, since carbonyl fluoride but not the fluorinating agent is readily hydrolyzed. Thus, a methylene chloride solution of **2** was added to a refluxing mixture of trifluoromethyl hypofluorite (bp −95 °C), water, and methylene chloride in a 0 °C bath. A 4 or 5 to 1 mixture of **3** and **4** was obtained, typically in 55% yield after distillation.

This method constitutes a satisfactory solution to the fluorination problem, but attempts were made to find better and cheaper reagents for the **2 → 3** transformation. Argentic fluoride[19] gave a nonvolatile mixture whose spectra suggested the presence of coupling products. Perchloryl fluoride[20] failed to react with the phenol at room temperature, but it did attack the sodium salt of **2** with results similar to those using argentic fluoride. Elemental fluorine in helium was bubbled into an acetonitrile solution of pentafluorophenol. At low conversions this method gave a 5:1 mixture of **3** and **4**, but it was not a practical solution because fluorine attacked the sensitive **3** as the 3:2 ratio increased. As noted above, stopping short of 100% conversion of **2** results in formation of **6**. Thus, one is caught between Scylla and Charybdis using elemental fluorine.

Bromine trifluoride is a highly potent fluorinating agent that has the virtue of being very inexpensive. It has enjoyed little use, probably because it generally yields horrible mixtures of reaction products. Bastock et al.[21] found that addition of bromine enhanced the reactivity of this reagent toward fluorinated benzenes. Conductivity studies by Quarterman et al.[22] have yielded evidence for a variety of ionic equilibria in bromine/bromine trifluoride mixtures, but the importance of these equilibria in nonpolar media is not known. In any event, bromine fluoride is present in such mixtures. Bastock's group found that bromine/bromine trifluoride mixtures attacked the two perfluorocyclohexadienes in different fashion, as shown in Scheme II. They rationalized their results with the hypothesis that net addition of F_2 can occur if the substrate ionization potential is low enough to permit radical cation formation but that otherwise BrF addition occurs via a bromonium ion.

Reaction of pentafluorophenol with bromine trifluoride at −78 °C in Freon 11 gave dienone **4** in very low yield and no detectable **3**. A similar experiment in which bromine (5%) was introduced along with the bromine trifluoride gave both **3** and **4** in 10% and 30% yields, respectively. In each experiment a halogen scavenger, 5-norbornene-2,3-dicarboxylic anhydride (chosen for its reactive double bond and low volatility), had been added after the reaction mixture had warmed to room temperature. IR measurements indicated, however, that much **3** had been lost upon
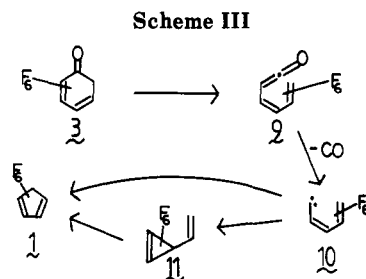
warming in the latter experiment. Addition of the norbornene derivative before warming failed to solve the problem, and it was found that destruction of **3** continued at room temperature even in the presence of excess scavenger. Since the norbornene double bond is surely more nucleophilic than the double bonds of **3**, these observations suggested that *ionization* rather than electrophilic attack might be the reason for the demise of dienone **3**.

Accordingly, naphthalene was tried as a quencher on the basis that its ionization potential should be lower than that of **3**. Addition of 0.5 equiv of naphthalene at −78 °C immediately after completion of the reaction transformed the red solution into a virtually black one. After a 0.5-h the mixture turned red again, and the catalytic amount of bromine remaining in the mixture was scavenged with the norbornene derivative. Dienones **3** and **4** were isolated in 50% yield in the ratio 2:3, a dramatic improvement over previous attempts. Finally, it was discovered that safrole (with its electron-rich benzene ring) is a more efficient quencher which also plays the role of bromine scavenger. Optimum conditions and results are presented in eq 1. In

(1)
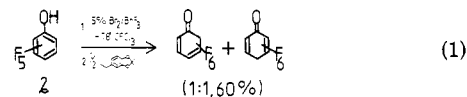
carrying out this reaction one must be cautious in handling bromine trifluoride, an extremely vigorous oxidizing agent, and in quenching the reaction, a very exothermic process.

In summary, two satisfactory procedures for transforming pentafluorophenol into hexafluorocyclohexa-2,4-dienone have been developed, one employing trifluoromethyl hypofluorite and the other bromine trifluoride/5% bromine. Total yields of the 2,4- and 2,5-dienones are comparable by the two methods, but the former enjoys the advantage of a much higher ratio of 2,4- to 2,5-product. On the other hand, the latter method has the virtue of using a fluorinating agent which costs about 5% as much per mole as trifluoromethyl hypofluorite.

Pyrolysis of the Hexafluorocyclohexadienones. Our optimism that dienone **3** could be induced pyrolytically to ring contract with decarbonylation was based both on analogy[23] to the *o*-quinone decarbonylations cited earlier and on mechanistic grounds. Electrocyclic ring opening would produce a conjugated α-fluoro ketene **9**.[24] This might be expected to decarbonylate readily, giving **10**, as judged from Krespan and England's finding that difluoro ketene apparently decomposes at 35 °C to carbon monoxide and difluorocarbene.[25,26] Cyclization of carbene **10**

(19) For the fluorination of benzene with this reagent, see: Zweig, A.; Fischer, R. G.; Lancaster, J. E. *J. Org. Chem.* **1980**, *45*, 3597–3603.

(20) Perchloryl fluoride is an electrophilic fluorinating agent which has been used for α-fluorination of ketones through their enolates.[13b]
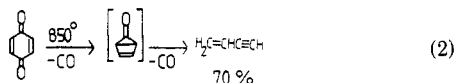
(21) Bastock, T. W.; Harley, M. E.; Pedler, A. E.; Tatlow, J. C. *J. Fluorine Chem.* **1975**, *6*, 331–335.

(22) Quarterman, L. A.; Hyman, H. H.; Katz, J. J. *J. Phys. Chem.* **1957**, *61*, 912–917.

(23) Further analogy is found in the formation of furan upon pyrolysis of 2-pyrone. Brent, D. A.; Hribar, J. D.; DeJongh, D. C. *J. Org. Chem.* **1970**, *35*, 135–137.

(24) 2-Pyrones and their sulfur analogues have been shown to interconvert thermally via electrocyclic ring opening, 1,5-shift of hydrogen and electrocyclic ring closure. Pirkle, W. H.; Turner, W. V. *J. Org. Chem.* **1975**, *40*, 1617–1620, 1644–1646.

(25) Krespan, C. G.; England, D. C. *J. Org. Chem.* **1968**, *33*, 816–821.

(26) Ketene decarbonylation has also been suggested as the pathway for CO loss in the pyrolysis of 2-pyrone to furan. Pirkle, W. H.; Seto, H.; Turner, W. V. *J. Am. Chem. Soc.* **1970**, *92*, 6984–6985.

should yield cyclopentadiene **1** either directly or indirectly via ring expansion of initially formed hexafluorovinyl-cyclopropene (**11**)[27] (Scheme III).

In the event, flash vacuum pyrolysis of **3** in a quartz tube at 625 °C and 0.1 torr gave hexafluorocyclopentadiene in 80% yield. Since the remaining 20% took the form of nonvolatile material which remained in the pyrolysis tube, no purification of the diene was necessary. Diene **1** was identified by comparison of its infrared, mass, and ^{19}F NMR spectra with the literature values;[3] it dimerized readily at room temperature, as reported, to *endo*-dodecafluorotricyclo[5.2.1.0[2,6]]deca-3,8-diene.[2e] No cyclopropene **11** was observed under any of a variety of pyrolysis conditions, but there is no definitive evidence to rule out its intermediacy.

Since 2,5-dienone **4** invariably accompanies the desired **3** in our fluorination products, it would be a windfall if **4** could also be thermally decarbonylated to **1**. Hageman and Wiersum[28] found that pyrolysis of *p*-benzoquinone gave mainly vinylacetylene (70%), and they did not detect cyclopentadienone dimers in the pyrolysis products from either this quinone or chloranil (tetrachloro-*p*-benzoquinone). They interpreted the *p*-benzoquinone decomposition as shown in eq 2, offering no mechanism for the initial decarbonylation. As an analogy for the pyrolysis

$$\underset{O}{\overset{O}{\bigcirc}} \xrightarrow[-CO]{850°} \left[\underset{O}{\overset{O}{\bigcirc}} \right] \xrightarrow[70\%]{-CO} H_2C{=}CHC{\equiv}CH \qquad (2)$$

of **4** this reaction was not entirely discouraging, for loss of difluorocarbene from a 5-carbon intermediate should be much less facile than CO loss. In fact, dienone **4** gave diene **1** as the principal product upon flash vacuum pyrolysis, perhaps via the high energy diradical **12**. Not surprisingly, **4** is substantially more resistant to pyrolysis than **3**, yielding only 10% of the diene at 625 °C under conditions where decomposition of the 2,4-isomer was complete. At this temperature the reaction of **4** was fairly clean, giving recovered starting material, **1** and minor amounts of perfluorobenzene and two unidentified impurities. Flash vacuum pyrolysis at higher temperatures yielded more **1**, unfortunately at the expense of a higher proportion of the impurities. At 770 °C conversion was complete, but now **1** comprised substantially less than half of the product and its separation from the unidentified impurities is very difficult.[29]
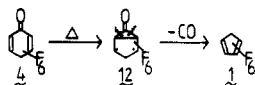
Since the 2,4- and 2,5-dienones differ in boiling point by only 3 °C (119 °C vs. 116 °C), it is not practical to separate them on a preparative scale. Thus, they were pyrolyzed as a mixture at 625 °C as described above to give **1** in ~80% yield from **3** and in ~10% yield from **4**. Starting with a 4:1 mixture of **3** and **4**, we obtained a 70%

Figure 2. Relative rates of dimerization of the chloropentafluorocyclopentadienes.

yield of hexafluorocyclopentadiene in 92–95% purity. No separation step to remove unreacted **4** was necessary since **4** can be intercepted by a –78 °C trap while **1** passes on to a –196 °C trap. The overall yield of diene from pentafluorophenol was 38%.
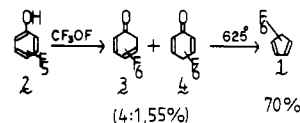
The easy separation of **1** and **4** suggested that the diene yield might be improved by a recycling procedure. After an initial pass, the sample reservoir at the front end would be replaced by sequential –78 °C and –196 °C traps like those at the other end. Now unreacted **4** could be returned through the hot tube by warming the –78 °C trap. Repetition would lead to continuing accumulation of **1** in both liquid nitrogen traps. In practice this scheme was successful, but the gain in yield was offset by the difficult-to-separate impurities which accompany **1** in the pyrolysate from **4**. Thus the procedure described in the preceding paragraph is the method of choice.

Related Pyrolyses. 6-Chloropentafluoro-2,4-cyclohexadienone (13). Pentafluorophenol reacts with *tert*-butyl hypochlorite in carbon tetrachloride to give this dienone in 70% yield, contaminated with minor amounts of the 2,5-isomer.[31] By analogy to the **3** → **1** transformation, pyrolysis of **13** would be expected to yield 5-chloropentafluorocyclopentadiene (**14**). This diene has been prepared in two steps from perchlorocyclopentadiene by Banks et al. (via the pentachloro fraction, Scheme I), but in extremely low yield.[32]

The compound is potentially important as a source of the pentafluorocyclopentadienyl ligand in organotransition-metal chemistry. Nucleophilic displacement of chlorine from **14**, e.g., by an organometallic anion, should be far more feasible than displacement of a geminal fluorine in **1**. Carbon–fluorine bond strengths are much greater than those of the corresponding carbon–chlorine bonds, and in this case the difference is enhanced by the *gem*-fluoro effect (the pronounced bond-strengthening effect which accompanies the accumulation of fluorines on the same carbon).[33] As a consequence, nucleophilic attack on **1** tends to cause displacement of a *vinyl* fluorine (by addition/elimination) rather than a geminal one (by the S_N2' or S_N2 mechanism).[34]

Flash vacuum pyrolysis of 6-chloropentafluoro-2,4-cyclohexadienone (**13**) at 650 °C and 0.1 torr gave chloropentafluorocyclopentadienes in 60% yield. GC/MS and IR analysis supported the structure assignment. The

(27) Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 315, 316. Analogy is also drawn here to the vinylcyclopropane rearrangement. See, for example: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 81–87.

(28) Hageman, H. J.; Wiersum, U. E. *Chem. Ber.* **1973**, *9*, 206–208; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 333–334.

(29) The posutlated intermediate **12** looks like a biradical formed in a photochemical di-π-methane rearrangement.[30] Accordingly, a single attempt was made to decarbonylate **4** photochemically. Irradiation in the gas phase with 254-nm light transformed **4** into a mixture of unidentified products, none of which was hexafluorocyclopentadiene.

(30) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed. Academic Press: New York, 1980; Vol. 3, pp 131–164.
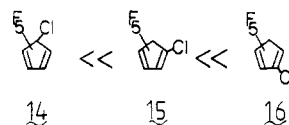
(31) Denivelle, L.; Huynh-Anh-Hoa *Bull. Soc. Chim. Fr.* **1974**, 2171–2174.

(32) Banks, R. E.; Bridge, M.; Haszeldine, R. N.; Roberts, D. W.; Tucker, N. I. *J. Chem. Soc. C* **1970**, 2531–2535. Chen et al. reported "good results" in the reductive dechlorination step using chromous chloride but gave no details or yields: Chen, T.; Graf, F.; Gunthard, Hs. H. *Chem. Phys.* **1983**, *75*, 165–173.

(33) Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron* **1982**, *38*, 2415. Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663.

(34) For example, the reaction of cyclopentadienedicarbonyliron anion with **1** yields the 1-pentafluorocyclopentadienyl derivative. Soelch, R. R.; Doig, S., unpublished results from this laboratory.

^{19}F NMR spectrum revealed the presence of two isomers in the ratio 2.3:1, and the major component was identified as the 1-chloro compound (15) by comparison with the literature NMR data.[32] Four signals (area ratio, 2:1:1:1) in the same regions of the spectrum indicated that the other isomer was the unknown 2-chloropentafluorocyclopentadiene (16). *None* of the desired isomer 14 was detected. Since their gas chromatographic behavior was virtually identical, 15 and 16 were not separated directly.

Both dimerized readily, but the 2-chloro isomer was strikingly more labile. When a 20% solution of a 2.3:1 mixture of 1- and 2-isomers was allowed to stand at –5 °C for 3 days, NMR analysis showed that all of the latter had dimerized, but 80–90% of the former remained (as determined by using Freon 11 as an internal area standard). This observation made purification of 15 easy because of the great difference in volatility between 16 and its dimer. Interestingly, Banks et al. were able to purify 5-chloropentafluorocyclopentadiene containing the 1-isomer by allowing the latter to dimerize; here also the difference in dimerization rates is large. Thus, the dimerization rate difference between 14 and 16 is quite impressive (Figure 2), and were are not able to account fully for the relative rates in the 14–16 series at this time.

Pyrolysis of dienone 13 at 550 °C (as in the original experiment, but 100 °C lower) gave the two chloropentafluorocyclopentadienes in only 40% yield, but the ratio of 15 to 16 was again 2.3:1 and none of the 5-chloro isomer was detected. Indeed, pyrolysis of a sample of 15 at 550 °C gave the same mixture of 15 and 16, demonstrating that the isomers equilibrate under the reaction conditions. Presumably, decarbonylation of 13 leads initially to the desired 14, which equilibrates with the other two isomers. One would expect [1,5] sigmatropic shift of chlorine to be the most facile rearrangement pathway for 14, but this process is degenerate and therefore not observed. The corresponding shift of the 5-fluorine would yield 15, however, and a repetition of the reaction would give 16. We favor this mechanism for the equilibration.
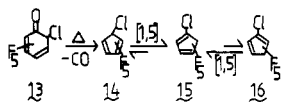

Given that the reaction is under themodynamic control, the failure to observe 14 is to be expected. Both 15 and 16 enjoy stabilization by the *gem*-fluoro effect,[33] while 14 does not. On the basis that 5% as much 14 as 15 would have been detected, we conclude that the free energy difference between these isomers is at least 4.9 kcal./mol at ~550 °C. Since Banks prepared 14 in a flow system at 430 °C, equilibration among the chloropentafluorocyclopentadiene isomers clearly does not become rapid until the temperature is very high.

Tetrafluoro-*o*-benzoquinone (17). Pyrolysis of this compound should give the known tetrafluorocyclopentadienone (20)[35] by analogy to the pyrolytic decarbonylations of the parent *o*-quinone, tetrachloro-*o*-benzoquinone, and the two cyclohexadienones discussed above. The present route to this reactive orange ketone is a quite efficient one, but it requires four steps from hexafluorobenzene and is limited in scale. Hence the prospect of a new route to 20 was appealing.

Unfortunately, presently available methods for preparing *o*-quinone 17 leave much to be desired. The compound can be made in four steps from hexafluorobenzene

but in less than 10% yield.[36] It is also available as a 1:1 mixture with the para isomer 18 (fluoranil) in 80% combined yield by the reaction of pentafluorophenol (2) with nitric acid.[37] This reaction yields 4-nitropentafluoro-2,5-cyclohexadienone (19), which slowly decomposes to the dienones, it is believed, via pentafluorophenoxy and nitro radicals. We attempted to find conditions for oxidation
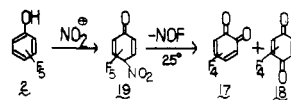

of 2 which would give higher yields of the *o*-quinone. Encouraged by Crivello's oxidation of pentachlorophenol to tetrachloro-*o*-benzoquinone in 80% yield using trifluoroacetyl nitrate generated in situ,[38] we followed the same procedure with 2 but obtained a mixture containing pentafluorophenyl trifluoroacetate plus a little fluoranil.[39] The method was modified by first preparing the trifluoroacetyl nitrate and then adding 2 in methylene chloride at –78 °C. The resulting light yellow solution contained nitrodienone 19, which decomposed over several hours at room temperature to a 2:1 mixture of the *o*- and *p*-quinones. The same nitrodienone was produced by oxidation of 2 with the mild nitrating agent *N*-nitro-*s*-collidinium tetrafluoroborate[40] at room temperature. In this case decomposition of 19 in methylene chloride gave a 5:4 mixture of the *o*- and *p*-quinones, but it was discovered accidentally that the ratio increased to 3:1 if 20 mol % of 2 was present during that decomposition. Pentafluorophenol was consumed in this reaction. In the last analysis, however, we were able neither to improve significantly upon the yield of 17 obtained by nitric acid oxidation nor to separate the quinone isomers. The *o*-quinone polymerizes readily at room temperature.[37]

Despite these problems, the original objective of preparing tetrafluorocyclopentadienone (20) was achieved by using a mixture of the two quinones. Flash vacuum pyrolysis of a 1:4 mixture (17–18) at 530 °C and 25 mtorr gave 20 in about 70% yield based on 17. The dienone was easily separated from accompanying fluoranil by vacuum transfer. It was identified by its gas-phase infrared spectrum and by the ^{19}F NMR spectrum of its rapidly formed dimer.[35] Fluoranil was found to be resistant to pyrolysis under these conditions even when the temperature was raised to 735 °C.
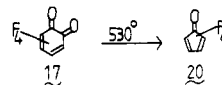
A Ring-Expansion Route to Hexafluorocyclopentadiene. Sargeant and Krespan found that tetrafluorocyclopropene adds almost quantitatively to tetrafluoroethylene at elevated temperatures to give octafluorocyclopentene, presumably via the bicyclopentane.[41]

(35) Grayston, M. W.; Saunders, W. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 413–414.
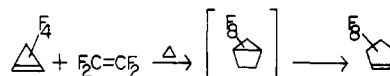
(36) Burdon, J.; Damodarin, V.; Tatlow, J. *J. Chem. Soc.* **1964**, 763–765.

(37) Shteingarts, V. D.; Budnik, A. G.; Yakobson, G. G.; Vorozhtosov, N., Jr. *Zh. Obshch. Khim.* **1967**, *37*, 1537–1540.

(38) Crivello, J. V. *J. Org. Chem.* **1981**, *46*, 3156–3063.

(39) We thank Roy F. Waldron, who carried out the initial experiments with this reaction.

(40) Olah, G. A.; Narrang, S. C.; Pearson, C. C.; Cupas, C. A. *Synthesis* **1978**, 452–453.

(41) Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415–419.

This suggests the possibility of incorporating a more reactive halogen into the olefin in order to prepare a cyclopentene which could be reductively dehalogenated to hexafluorocyclopentadiene. We found that bromotrifluoroethylene also adds to tetrafluorocyclopropene at 170 °C to give a mixture of 4- and 3-bromocyclopentenes (**21** and **22**) in the ratio 84:16. A mixture is to be expected since the fluorine migration which accompanies cleavage of the central bond of the intermediate bicyclopentane can occur in either of two directions. The ^{19}F NMR spectrum
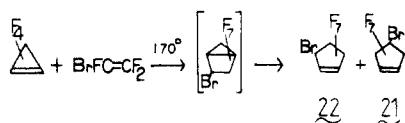
(CDCl$_3$) of the symmetrical isomer **21** comprises a subsplit AB quartet at δ 95.99 and 120.90, $J = 246$ Hz (F$_3$'s, F$_5$'s), and multiplets at δ 129.22 (quintet, F$_4$) and 149.06 (sextet, F$_1$,F$_2$). Allylic bromide **22** gives rise to a subsplit AB quartet at δ 57.76 and 60.76, $J = 183$ Hz (F$_4$'s), an incompletely resolved AB quartet at δ 114.49 and 116.27, $J = 200$ Hz (F$_5$'s), and multiplets at δ 122.28, 125.32 (F$_1$,F$_2$), and 166.37 (F$_3$). Not surprisingly, loss of Br in the mass spectrum is much more prominent for the allylic bromide **22** than for **21**. The relatively high reactivity of allylic bromine may also explain the small amount of **22** in the product, as much of it may have decomposed under the reaction conditions. The (unoptimized) yield of the bromide mixture after purification by gas chromatography was just 31%. Reduction of the mixture of **21** and **22** with zinc dust and zinc chloride in ethanol gave 1,2,3,3,4,5,5-heptafluorocyclopentene (**23**), the product of replacing bromine by hydrogen in **21**: ^{19}F NMR (ethanol) subsplit AB quartet, δ_A 109.5 (2 F), δ_B 115.0 (2 F) ($J = 256$ Hz), 152.1 (quintet, 2 F), 214.7 (subsplit doublet, 1 F) ($J_{H-F} = 48.8$ Hz); Ms, m/e 194 (M$^+$), 175 (M$^+$ – F), 144 (M$^+$ – CF$_2$), 125 (M$^+$ – CF$_3$), 93 (C$_3$F$_3^+$), 75 (base, C$_3$HF$_2^+$), 69 (CF$_3^+$).
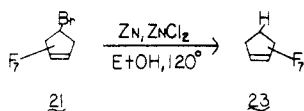
When the aprotic solvent diglyme was used, however, the zinc/zinc chloride combination smoothly reduced the bromide mixture to hexafluorocyclopentadiene (**1**), which was isolated in 98% purity and 92% yield.
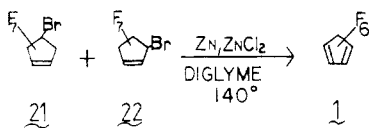
Because of the poor yield in the cycloaddition step and the fact that tetrafluorocyclopropene is not trivial to prepare, this route to **1** is not a practical alternative to the synthesis from pentafluorophenol described above. We believe that the latter route will make hexafluorocyclopentadiene more readily accessible to the chemical community than it has been to date.

Experimental Section

The ^{19}F NMR spectra were obtained on a JEOL FX-60Q Fourier transform instrument operating at 56.2 Mhz or on a Varian XL-300 Fourier transform spectrometer operating at 282.2 Mhz. Chemical shifts are reported in ppm upfield from internal trichlorofluoromethane (Freon 11). Mass spectra were measured by Rudy Zsolway on a Finnegan GC/EI-CI 4000 spectrometer. Analytical gas liquid chromatography was carried out with a Hewlett-Packard 5880A gas chromatograph using a flame ionization detector. Peak areas were determined by electronic in-

tegration and are uncorrected for differential detector response. Preparative GLC was done with a Hewlett-Packard 5750 chromatograph using a thermal conductivity detector. Melting points were determined in sealed Pyrex capillaries and are uncorrected. The term "static" vacuum transfer refers to a closed system distillation, while "dynamic" vacuum transfers were done by pumping a sample to or through a cold trap. Vacuum transfers were carried out from room temperature to –196 °C unless noted otherwise.

Pyrolysis tubes were prepared by wrapping a coil of nichrome wire (22 gauge, 1 ohm/ft, Ogden Mfg. Co.) around a tube made of Pyrex, Vycor, or fused quartz. An iron–constantan thermocouple was placed against the outside of the tube in the center of the zone to be heated, without touching the nichrome wire. The entire tube was then insulated with three layers of asbestos tape. Temperatures were controlled with variacs and were monitored by a 1000 °C temperature readout (Omega Engineering).

All compounds were prepared under nitrogen (dried with a train containing concentrated sulfuric acid, potassium hydroxide, and Drierite) except when indicated otherwise. All solvents and reagents were reagent grade, and solvents were dried according to the literature procedures.[42] Hexafluorobenzene was purchased from the Fairfield Chemical Co., trifluoromethyl hypofluorite and Freon 11 from PCR Research Chemicals, Inc., bromotrifluoroethylene from the Pierce Chemical Co., argentic fluoride from Alfa Products, fluorine/helium (1:1) from the Matheson Gas Co., and both bromine trifluoride and perchloryl fluoride from Ozark-Mahoning, a division of Pennwalt. Zinc dust, zinc chloride, and Halocarbon 25-5S grease were obtained from Fisher Scientific Co.; dipentene came from Eastman. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

Fluorination of Pentafluorophenol (2) with Trifluoromethyl Hypofluorite. A. Trifluoromethyl hypofluorite (3.2 g, 31 mmol) was transferred via a stainless steel high-pressure manifold to a tared steel cylinder (approximately 400-mL volume) cooled to –196 °C. This gas cylinder was then connected by Tygon tubing to a trap via a tee which allowed for introduction of nitrogen. The trap was attached to a gas bubbler (coarse fritted disc) which extended well below the surface of the magnetically stirred 10% solution of the phenol (2.6 g, 14 mmol) in Freon 11 in a tube reactor (400 × 25 mm o.d.). The reactor outlet was connected to a bubbler via an acetone/dry ice cooled trap. After the apparatus had been flushed with nitrogen, trifluoromethyl hypofluorite was slowly bubbled into the phenolic solution over an 8-h period. When gas evolution had ceased the solvent was distilled at atmospheric pressure under nitrogen and products (2.6 g) were then collected at 25–26 °C (12 torr) in a dry ice-cooled receiver: GC (column, 12.5 × $^1/_8$ in., 5% SF-96 on Chromasorb W HP; oven, 50 °C; flow rate, 20 mL/min; injection temperature 110 °C) retention time 1.91 (hexafluoro-2,5-cyclohexadienone), 2.07 min (hexafluoro-2,4-cyclohexadienone); IR (neat) 1740 and 1660 ($\nu_{C=C,C=O}$), 1410, 1360 and 1330 cm^{-1} (ν_{C-F}); ^{19}F NMR (CDCl$_3$, hexafluoro-2,5-cyclohexadienone[11]) 115.4 (F$_4$'s), 144.6 (F$_3$, F$_5$), 151.7 (F$_2$, F$_6$), (CDCl$_3$, hexafluoro-2,4-cyclohexadienone[11]) 110.9 (2 F), 129.6 (1 F), 150.4 (1 F), 152.7 (1 F), 158.4 (1 F). A sample of hexafluoro-2,4-cyclohexadienone was purified by preparative gas chromatography: column, 10 ft × 0.25 in. 10% SF-96 on Chromasorb-W HP; oven temperature 60 °C; injection temperature 165 °C; detector (TCD) at 190 °C; retention time 2.5 min. IR (gas phase) 1740 and 1670 ($\nu_{C=C, C=O}$), 1410, 1360, and 1330 cm,–,1 ($\nu_{C-C,C=O}$), 1410, 1360, and 1330 cm^{-1} (ν_{C-F}). Continuing the distillation gave a small amount of pentafluorophenyl 3-(pentafluoro-2,4-cyclohexadienyl) ether, bp 110–115 °C (12 mm). This solid was statically sublimed [30 °C (0.05 mm)] to give off-white, flaky crystals: mp 55–57 °C; IR (KBr) 1745, 1735, 1650, and 1640 ($\nu_{C=C, C=O}$), 1530 cm^{-1} (ν_{ArC-F}); ^{19}F NMR (CDCl$_3$) 110.9 (2 F, octet), 149.8 (1 F), 151.2 (1 F), 155.3 (3 F), 159 (1 F), 160.5 (2 F); MS, m/e 366 (M$^+$), 155 (base, C$_5$F$_5^+$). Anal. Calcd for C$_{12}$F$_{10}$O$_2$: C, 39.36; F, 51.89. Found: C, 39.08; F, 51.42. The same ether is formed instantly at room temperature by adding an equal volume of 10% NaHCO$_3$ to a 10% solution of equimolar amounts of hexafluoro-2,4-cyclohexadienone and pentafluorophenol in methylene chloride.

(42) Gordon, A. J.; Ford, R. A., Eds. "The Chemist's Companion"; Wiley: New York, 1972.

B. Trifluoromethyl hypofluorite (5.2 g, 50 mmol, 2 equiv) was condensed onto ice (0.9 g, 50 mmol) and methylene chloride (80 mL) at −196 °C in a 250-mL three-neck flask fitted with dry ice condenser and dropping funnel. The condenser was maintained throughout the experiment at −130 °C (pentane/liquid nitrogen). After this addition the CF_3OF inlet adapter was replaced with a glass stopper; and the solution was allowed to warm in an ice bath. Pentafluorophenol (4.4 g, 24 mmol) in 55 mL of methylene chloride was added rapidly (over 10 min) to the CF_3OF solution as soon as it could be stirred. This mixture was allowed to stir for 1 h longer at 3 °C and then dried with $MgSO_4$; the solvent was distilled under nitrogen. The products were distilled at 20 mm up to 55 °C and caught in a dry ice cooled receiver. Redistillation under nitrogen at atmospheric pressure gave 2.62 g, of which 93% by GC was a mixture of hexafluorocyclohexadienones (52% yield, bp 110–119 °C) in a ratio of 4:1 (2,4- to 2,5-isomer).

Purification of Bromine Trifluoride. A bromine trifluoride cylinder was connected to a vacuum system through two dry U-traps, one at −78 °C (fitted with ground-glass stopcocks, packed with Pyrex helices and tared) and the other at −196 °C. Halocarbon 25-2S grease[42] was used to lubricate ground-glass connections, but even this inert material was attacked by the gaseous BrF_3 at a substantial rate. With the cylinder maintained at 25–30 °C, the desired amount of fluorinating agent was transferred to the −78 °C trap at 0.1 mm. The BrF_3 cylinder was isolated and the heterogeneous red and yellow trap contents were allowed to warm, still under vacuum, in order to transfer volatile impurities (particularly BrF) to the −196 °C trap. When all of the red impurities were removed the BrF_3 trap was weighed. It was important to keep this purified reagent cold (dry ice) until it was used so that it would not react with the stopcock grease. Teflon stopcocks probably can also be used, but neat *liquid* BrF3, like ClF3, has been found to react with Teflon at an appreciable rate.

Fluorination of Pentafluorophenol (2) with Bromine Trifluoride. Bromine (0.24 g, 1.48 mmol, 5 mol %) was dissolved in $CFCl_3$ (40 mL) and frozen (−196 °C) in a three-neck 250-mL round-bottom flask equipped with Teflon stir bar, pressure-equalizing dropping funnel, and connection via a bubbler to a nitrogen tank. After this reaction vessel had been evacuated, purified BrF_3 (4.06 g, 29.6 mmol) was condensed in. The mixture was allowed to thaw, and dry nitrogen was bled in. The suspension was allowed to warm only enough so that it could be efficiently stirred and was then recooled to −78 °C. Pentafluorophenol (5.45 g, 29.6 mmol) dissolved in $CFCl_3$ (40 ml) was placed in the dropping funnel and added dropwise through the center neck during 25 min to the fluorinating suspension. Distilled safrole (2.4 g, 14.8 mmol) dissolved in 5 mL of $CFCl_3$ was then immediately added over about 2 min to quench the reaction. **NOTE:** *This quenching is very exothermic and should be done more slowly in larger scale reactions to avoid a potential explosion hazard!* After 10 min at −78 °C the reaction mixture was allowed to warm to room temperature. The orange-yellow solution (with dark solid) turned purple after about 30 min at room temperature. (The species responsible for the purple color was probably derived from safrole since reactions quenched with naphthalene remained orange-yellow.) The Freon-11 was distilled under nitrogen and then the products were distilled at 0.1 mm into a −196 °C receiver with the head temperature reaching 35 °C. At this point GC analysis revealed that no dienones remained in the pot. The products were redistilled under nitrogen through a 6-in. vacuum-jacketed Vigreux column to give a mixture which was 92% cyclohexadienones 3 and 4 (7% "C_6F_7BrO"), bp 110–116 °C. The yield of 2,4-dienone 3 was 1.95 g, 9.64 mmol, 33%; that of 2,5-dienone 4 was 1.68 g, 8.31 mmol, 28%.

In an earlier series of runs in which the reaction mixture had been allowed to warm without quenching, the "C_6F_7BrO" noted above comprised a greater share of the product. The fact that yields of this materal and 3 varied inversely suggests that it was formed by BrF addition to 3. This substance, which had a substantially longer GC retention time than the dienones, was isolated by preparative GC as a colorless, volatile liquid: GC (column, 10 ft × 0.25 in. 10% SF-96 on Chromasorb-W HP; oven, 65 °C/4 min, program rate 20 °C/min, final temperature 150 °C/10 min; injection temperature 150 °C) retention time 5.25 min; IR (gas phase) 1768 and 1711 ($\nu_{C=C, C=O}$), 1368 and 1334 cm^{-1} (ν_{C-F}); ^{19}F

NMR ($CDCl_3$) 92.8 (0.6), 97.9 (1.0), 100.1 (0.6), 105.2 (1.0), 115.6 (1.1), 121.4 (1.8), 126.6 (0.6), 132.5 (1.7), 143.7 (1.6); MS, (C_6F_7BrO) m/e (relative intensity) 302 (M$^+$, 0.43), 300 (M$^+$, 0.56), 221 (base, $C_6F_7O^+$). From its ^{19}F NMR spectrum it is clear that the "C_6F_7BrO" is not a single isomer.

Hexafluorocyclopentadiene (1) from Cyclohexadienones 3 and 4. A. Flash vacuum pyrolysis at 600 °C (0.1 mm, 8 × 950 mm quartz tube) of hexafluorocyclohexadienones (0.58 g, 2.8 mmol) in a ratio of 5:1 (2,4-dienone 3 to 2,5-dienone 4), evaporated from a reservoir at room temperature, gave 0.52 g of volatile products which were condensed at −196 °C. This mixture contained cyclopentadiene 1 (0.39 g, 2.2 mmol, 78% yield), 4 (ca. 0.11 g), and minor unidentified byproducts.

B. Flash vacuum pyrolysis (0.04 mm, 8 × 1000 mm quartz tube) at 625 °C of 2,4-dienone 3 (3.64 g, 18 mmol) and 2,5-dienone 4 (1.56 g, 7.7 mmol), evaporated from a room-termperature reservoir, gave 4.31 g of volatile products. The products were caught in a Pyrex-helix-filled U-trap cooled to −196 °C. After vacuum transfer, distillation under 1 atm nitrogen into a −78 °C receiver gave 2.4 g (53% yield, 95% pure by GC and ^{19}F NMR) of hexafluorocyclopentadiene: bp 27–32 °C; GC (column, 12.5 ft × $^1/_8$ in. 5% SF-96 on Chromasorb-W HP; oven 50 °C; flow rate 8 mL min) retention time 1.77 min; IR (vapor) 1770 ($\nu_{C=C}$), 1410 and 1350 cm^{-1} (ν_{C-F}); ^{19}F NMR ($CDCl_3$) 135.9 (2 F), 151.3 (2 F), 167.9 (2 F); MS, m/e 174 (M$^+$), 155 (M$^+$ − F), 143 (M$^+$ − CF), 124 (base, M$^+$ − CF$_2$), 117, 105, 93, 86, 74, 69, 55.[3] The pot contents (1.91 g) were dienone 4 (1.64 g, 32%) and cyclopentadiene 1 (0.27 g, 6% yield). This workup can be avoided by isolating the products in two traps at −78 and −196 °C, the latter trapping pure 1.

Pyrolysis of 6-Chloropentafluoro-2,4-cyclohexadienone (13). Vacuum flow pyrolysis (0.1 mm, 8 × 500 mm quartz tube) at 650 °C of 13 (1.68 g, 7.7 mmol) gave, after a static vacuum transfer, a light yellow volatile liquid (1.66 g) which contained 1- and 2-chloropentafluorocyclopentadiene (1.02 g, 5.4 mmol, 70% yield by GC) in a ratio of 2.3:1. This product was partially vacuum transferred statically, giving 630 mg of yellow condensate which was 86% chlorocyclopentadienes and 1.13 g of residue which was 56% chlorocyclopentadienes by GC. These data were obtained on the purer fraction: GC (column, 12.5 ft × $^1/_8$ in. 5% SF-96 on Chromasorb-W HP; oven 40 °C; flow rate 8 mL/min) retention time 1.8 min (shown by preparative GC to contain both chloropentafluorocyclopentadienes 15 and 16); IR (vapor) 1810 (w), 1760 (s), 1730 (w), and 1695 (s) ($\nu_{C=C}$), 1410 and 1360 cm^{-1} (ν_{C-F}); ^{19}F NMR [reported for 1-chloropentafluorocyclopentadiene[32]] ca. 131 (3 F), 151 (1 F), 158 (1 F) [found (CD_3CN)] 129.4 (1 F), 132.0 (2 F), 149.4 (1 F), 160.7 (1 F), [2-chloropentafluorocyclopentadiene (CD_3CN)] 134.8 (2 F), 145.4 (1 F), 148.1 (1 F), 170.8 (1 F); MS, m/e (relative intensity) (M$^+$, 10.5), 190 (M$^+$, 40.9), 155 (base, M$^+$−Cl). This fraction stood at room temperature for 6 h and was then stored at −78 °C for 2 days. ^{19}F NMR revealed that all of the 2-chloro isomer had dimerized while most of the 1-chloro isomer remained. A partial static vacuum transfer (halted when a yellow component condensed in the cold trap) gave 253 mg of a slightly yellow liquid which contained 90% pure 1-chloro isomer 15 by ^{19}F NMR.

Equilibration of Chlorocyclopentadienes 15 and 16. Vacuum flow pyrolysis at 550 °C (0.1 mm, 8 × 450 mm quartz tube) of 1-chloropentafluorocyclopentadiene (0.253 g, 1.3 mmol, 90% pure) gave a volatile product, which was trapped at −196 °C. Static vacuum transfer yielded a slightly yellow liquid (0.205 g, 1.1 mmol, 90% pure), a mixture of the 1- and 2-chloro isomers in a ratio of 2.3:1.

Tetrafluorocyclopentadienone (20): Pyrolysis of Tetrafluoro-o-benzoquinone (17). Flash vacuum pyrolysis at 525 °C (0.025 mm, 7 × 400 mm Vycor tube) of tetrafluoro-o-benzoquinone (17) and fluoranil (18) (1:4, 0.107 g, 0.59 mmol) gave an orange mixture which was trapped at −196 °C. A gas-phase IR spectrum showed absorptions in the 1800–1750 cm^{-1} region for cyclopentadienone 20[35] and also strong absorptions in the 1980–1960 cm^{-1} region (perhaps due to perfluorocyclopropenes). The volatile products (0.024 g) were statically transferred to a storage bulb and stored for 3 days in vacuo at room temperature. ^{19}F NMR [CD_3CN, tetrafluorocyclopentadienone dimer, found (reported[35])] 118.8 (119.0), 129.5 (129.5), 141.9 (141.8), 142 (142.2), 184.0 (184.0), 184.7 (184.7), 217 (216.2). This compound accounted for half of the fluorine in the sample. Decarbonylated dimer[35]

was also present, as was another compound giving a very high field resonance (ν 212.6) suggestive of bridgehead fluorine. The dimer and its decarbonylation product were formed in about 70% yield from quinone **17**.

Bromoheptafluorocyclopentenes 21 and 22. To a heavy-walled Pyrex ampoule (10 × 200 mm, 5 mm i.d.) was added 85 μL of dipentene; the bomb was cooled to –196 °C and evacuated. Bromotrifluoroethene (2.67 g, 16.6 mmol) and tetrafluorocyclopropene (1.62 g, 14.5 mmol, prepared by the method of Sargeant and Krespan[41]) were introduced in vacuo and the bomb was sealed. It was heated at 170 °C in a tube oven for 7 h. After cooling, the bomb was opened and all volatiles were vacuum transferred into a side-arm flask with septum. Preparative GC on a 10 ft × 0.25 in. column containing 10% SF-96 on Chromasorb-W HP at 27 °C with a helium flow of 35 mL/min yielded 1.22 g (4.47 mmol, 31%) of C_5F_7Br. Anal. Calcd. for C_5F_7Br: C, 22.01; F, 48.71; Br, 29.28. Found: C, 22.10; F, 48.52; Br, 29.06.

3-Bromoheptafluorocyclopentene (16% of total C_5F_7Br) eluted at 7.95 min; bp 71 °C; IR (vapor) 1800 ($\nu_{C=C}$), 1400, 1293, 1175 cm^{-1}; MS, m/e 274 (M$^+$), 272 (M$^+$), 193 (M$^+$ – Br), 143 ($C_4F_5^+$), 93 (base, $C_3F_3^+$).

4-Bromoheptafluorocyclopentene (84% of total C_5F_7Br) eluted at 9.55 min; bp 72 °C; IR (vapor) 1767 ($\nu_{C=C}$), 1384, 1255, 1173 cm^{-1}; MS, m/e 274 (M$^+$), 272 (M$^+$), 193 (base, M$^+$ – Br), 143 ($C_4F_5^+$), 93 ($C_3F_3^+$). The ^{19}F NMR spectra of both isomers are reported in the text.

Hexafluorocyclopentadiene (1). To a 177-mL (6 oz)

Fischer–Porter glass bomb equipped with valve were added 20 mL of diglyme (freshly distilled from CaH$_2$), 0.11 g of zinc chloride, and 4.5 g (69 mmol) of activated[43] zinc dust. The contents were degassed in two freeze–pump–thaw cycles, and then 415 mg (1.52 mmol) of bromoheptafluorocyclopentene (84% 4-bromo and 16% 3-bromo isomer) was vacuum transferred into the bomb. The vessel was sealed, warmed to room temperature, and then immersed in a preheated 135 °C oil bath. After dropping to approximately 120 °C, the temperature was slowly raised to 140 °C and maintained there for 10 min. The bomb was removed from the bath and cooled; the more volatile components (approximately 1 mL) were transferred in vacuo to a distillation bulb. A bulb-to-bulb distillation into a flask containing 1.0 mL of o-dichlorobenzene yielded 245 mg (1.41 mmol, 92%) of hexafluorocyclopentadiene. The o-dichlorobenzene solution was used for all manipulations and storage (–25 °C) of the diene to minimize dimer formation. Gas chromatography revealed that the compound was 98% pure. GC, IR, and ^{19}F NMR data all matched those of hexafluorocyclopentadiene prepared by pyrolysis of hexafluoro-2,4-cyclohexadienone (3).

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Notes

Bridgehead Solvolytic Reactivity. A Unified Data Set To Test Molecular Mechanics

T. William Bentley* and Karl Roberts

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K.

Reactions at bridgehead carbon provide a unique opportunity to investigate structure/energy and structure/reactivity relationships.[1] Following earlier studies on synthesis and kinetics,[2,3] Gleicher and Schleyer[4a] applied empirical force field (molecular mechanics) calculations to correlate and predict bridgehead reactivities over 12 orders of magnitude. At this early stage in these developments, cautionary comments about the preliminary nature of the force field were made, and it was implied that the solvolysis data did not cause significant ambiguities. Later, Bingham and Schleyer[5] correlated bridgehead re-

activities over 18 orders of magnitude. These pioneering studies[4,5] established molecular mechanics as a valuable method for studies of structure/reactivity relationships.

There was one very surprising feature in Bingham and Schleyer's study.[5] Separate correlation lines of substantially different slopes were calculated for chlorides, bromides, tosylates, and triflates. It was predicted that the tosylate/bromide rate ratio, typically over 1000, would be less than unity for very unreactive substrates. In a later discussion of these results, it was stated that there were "really threatening obstacles of internal return, solvation energies, nonclassical structures, etc., which plague studies of carbonium ions."[6] Thus, the emphasis appeared to have shifted from difficulties in parameterizing the force field (particularly for carbocations) to possible ambiguities in the interpretation of the solvolysis data.

More recently there has been considerable progress in mechanistic studies of solvent and leaving-group effects on S_N1 reactions.[7] We now show that consistent corrections can be made for changes in solvents and leaving groups, leading to a unified data set spanning 22 orders of magnitude in reactivity. Recent thermochemical data for carbocations in solution[8] and in the gas phase[9] will also

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