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The Coupling Reactions of Alicyclic 1, 2-Dihalopolyfluoroolefins with Copper

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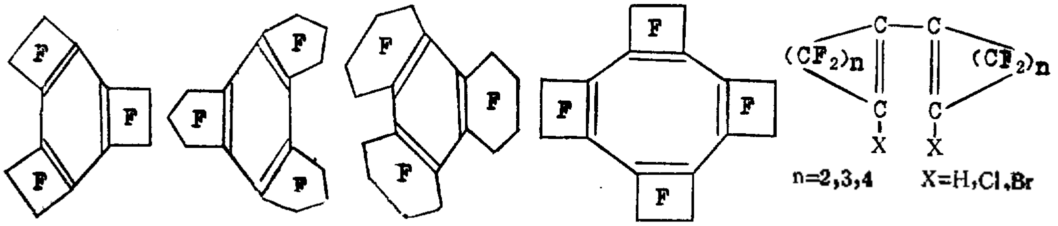
Abstract This paper reports the reaction of monoiodoperfluorocycloalkense with alkyl lithium and activated copper respectively resulting in various coupling products. Of particular interests are compounds of the following composition.



The physical properties of the various compounds are given along with a discussion relating to the mechanistic pathways involved in the coupling reactions.

Introduction

Prior to the successful application of the Ullmann reaction to the synthesis of polyfluorobicyclobutenes, no general synthetic route to these corpounds were available. The present study is concerned with a study arriving at a useful synthesis of polyfluorobicyclobutenes through reductive coupling and a cross coupling reaction and an investigation into the chemistry[1] of these coupled products.

Intermolecular dehalogenation of polyfluoroalkyl and alkenyl halides has been achieved by Henne.[2] He reported that when $CF_3CF_2CF_2I$ is treated with zinc in acetic anhydride, a coupling resutls with the formation of C_6F_{14} in excellent yields. Similarly, $C_3F_3Cl_4Br_3$ is coupled to yield $C_6F_6Cl_8$ with equal facility, Conversely, CH_3CF_2Cl and $CHCl_2CF_2CF_2Cl$ each react in exceedingly poor yields: and $CCl_3CF_2CCl_2CCl_3$ undergoes customary dechlorination to $CCl_3CF_2CCl{=}CCl_2$. These results seem to indicate that doubling of the chain length might depend on a terminal-CF_2 or- CFClX group where X is bromine or iodine, at least for an efficient reaction to take place.

Miller(4) reported that highly fluorinated organozinc derivatives were obtainable in dioxane solution.

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[***] This work represents part of the research of S. K. C., for his Ph. D. degree at the University of Colorads Bouldes Colo., 80302 U. S. A.

In 1955, Henne and Postelnek[5] synthesized perfluorinated butadiene. They treated 1, 2, 2-trifluoro 1, 2-dichloroiodoethane with zinc in acetic anhydride to obtain 1, 1, 2, 3, 4, 4-hexafluoro-1, 2, 3, 4-tetrachlor butane by chain length doubling, followed by dechlorination with zinc in alcohol to yield the desired perfluorobutadiene.

$$CF_2Cl\text{-}CFClI \xrightarrow[(CH_3CO)_2O]{Zn} CF_2Cl\text{-}CFCl\text{-}CFCl\text{-}CF_2Cl$$

$$\xrightarrow[ROH]{Zn} CF_2{=}CF-CF{=}CF_2$$

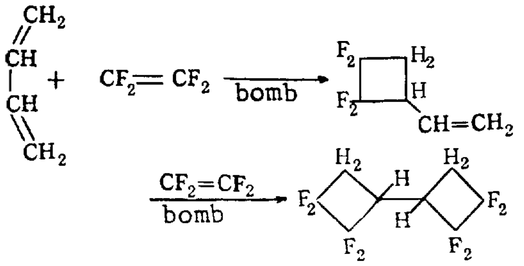
Tatlow and co-workes[6] also synthesized a large number of similar compounds. They prepared 1, 4-dichlorotetrafluorobuta-1, 3-diene by the action of 1-chloro-1, 2-difluoroiodoethylene with copper bronze kept at 145°C in a sealed tube for 24 hours.

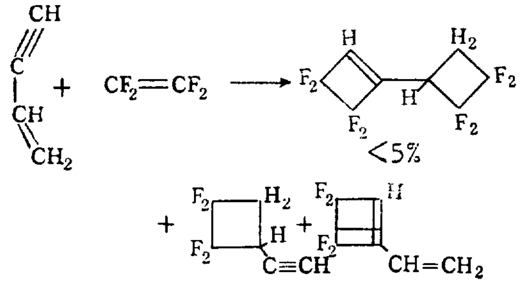
$$CClF{=}CFI \xrightarrow[145°/24\ hrs.]{Cu\text{-}Bronze} CClF{=}CF-CF{=}CClF$$

They also reported that the same olefin undergoes a cross coupling reaction with phenyl and pentafluoro-phenyl halides.

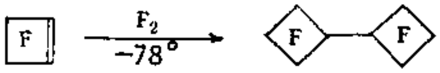
There are relatively few synthesis of polyfluorodicyclobutanes and dicyclobutanes and dicyclobutenes (hereinafter referred to as "dibox" compounds) reported in the literature. An adequate review of earlier work in this area has been compiled by Frank.[7,8]

Prior to Frank's work, no general pattern for the synthesis of polyfluorinated "dibox" compounds was available. Coffman, Barrick et al, (9) were the first to apply thermal cycloaddition toward this end. They reacted butadiene with excess tetrafluoroethylene in a bomb under autogenous pressure to obtain a 10-15% yield of 2, 2, 2', 2', 3, 3, 3', 3'-octafluorodicyclobutane. In addition they treated vinyl acetylene with tetrafluoro-ethylene to obtain the cycloaddition products indicated below.

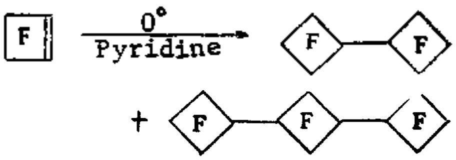




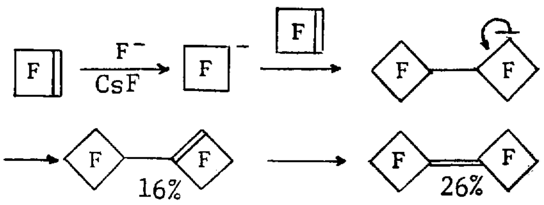
Shortly thereafter, Miller[4] accomplished the coupling of two hexafluorocyclobutene units in liquid fluorine at −78° C. to obtain perfluorodicyclobutane, an inert liquid.



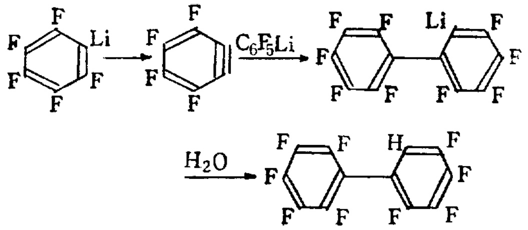
Pruett et al.[10] also described the reaction of aliphatic tertiary amines with hexafluorocyclobutene. They prepared a mixture of the dimer and trimer of hexafluorocyclobutane through the reaction of perfluorocyclobutene with pyridine at 0° C. The time required for these reactions varied from several hours to a period of weeks.



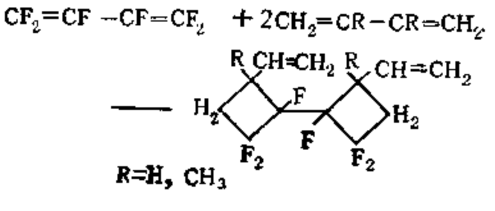
More recently, Young et al[11] found that with added cesium fluoride a rearranged product was obtained. They applied this reaction in the dimerization of hexafluorocyclobutene, probably perfluorocyclobutane anion was added to second hexafluorocyclobutene to give perfluorodibox compound.



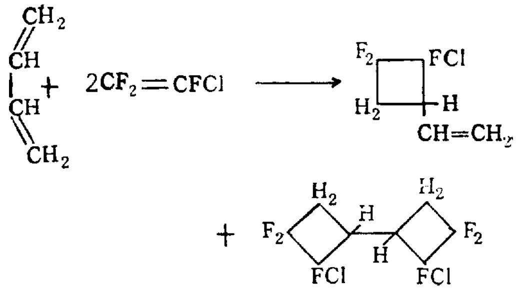
Fenton and Massey[12] also prepared 2-hydrononafluorobiphenyl from pentafluorobenzene. A mechanism, involving tetrafluorobenzyne as an intermediate, was proposed for the reaction. In an effort to understand the correct mechanism, an ether-hexane solution of pentafluorophenyllithium was allowed to warm to room temperature from −78° C, and after standing for 30 minutes, was hydrolysed with distilled water. 2-hydrononafluorobiphenyl was isolated in a fair yield which strongly suggested that at a convenient temperature pentafluorophenyllithium is converted partially to tetrafluorobenzyne which interacts with unconverted pentafluorophenyllithium to give (nonafluoro-2-biphenyl) lithium.



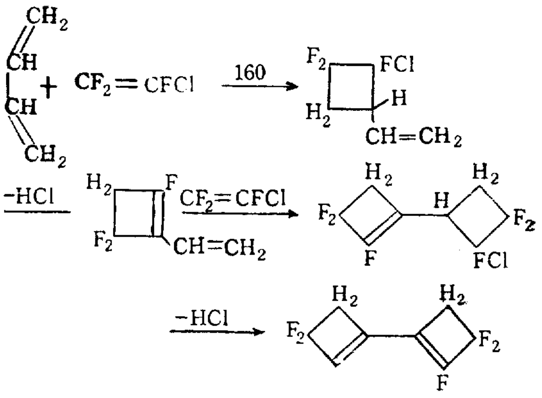
Sharts and Roberts[13] again applied the thermal cycloaddition reaction in treating isopropenyl acetylene with chlorotrifluoroethylene to give the two expected 1 : 1 aducts and less than 5 % of a "dibox" derivative. Similarly, Ryananova et al.,[14] resported 10–15% yield of 2 : 1 adducts from the thermal cycloaddition of 1 : 3-butadiene to perfluorobutadiene.



Frank[7,8] of this laboratory extended the knowledge of thermal cycloaddition of polyfluoroethylene in preparing cyclobutanes (a review has recently been published)[8] relating to the synthesis of "dibox" derivatives. In reacting 1, 3-butadiene with trifluorochloroethylene in an autoclave he isolated 5–10% of a 1 : 2 adduct, 2, 2′-dichloro-2, 2′, 3, 3, 3′, 3′-hexafluorodicyclobutane, in addition to the normal 1 : 1 adduct. Increasing the molar rato of trifluoroethylene did not improve the yield of the diadduct significantly.

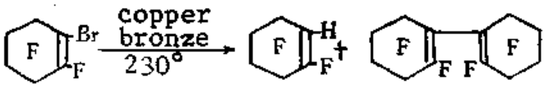


The following synthetic pathway ultimately proved most useful in the synthes of "dibox" compounds.

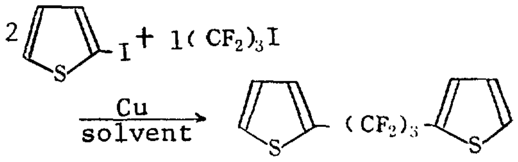


In view of these results, it is apparent that a logical pathway to polyfluorocyclobutene would involve thermal cycleaddition followed by dehydrochlorination.

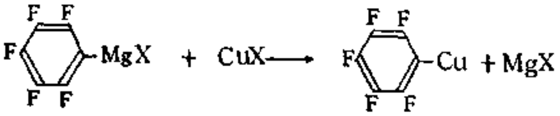
A study was also made by Tatlow and co-workers[6] and they described that two perfluorocyclicv inyl bromides, 1-bromononafluorocyclohexene[14] and 1-bromoheptafluorocyclopentene, underwent coupling with copper bronze. In treating 1-bromononafluorocyclohexene and copper bronze at 230° C. in a sealed pyrex tube for 48 hours, mixture of 1-H-nonafluorocyclohexene and perfluorobicyclohexenyl was obtained.



Fluoroalkyl substituted aromatic derivatives were first reported by White(15) by the cross coupling of 1, 3-diiodohexafluoropropane with 2-iodothiophene to yield the corresponding fluoroalkyl-substituted thiophene derivatives. The reaction takes place in polar aprotic solvent in the presence of powdered copper.



Recently, Cairncross and Sheppard[16] isolated several fluorinated organocopper compounds and found that they were highly soluble in organic solvents and thermally more stable than their hydrocarborn anologs. They prepared a solution of fluorinated aryl copper (1) compounde by the metathetical reaction of Grignard reagent with cuprous halide in ether.

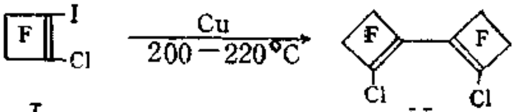


They also found that fluorinated arylcoppers pyrolyzed readily to biphenyls and copper. When the thermal coupling reactions were run in solvents and reagents known to react with free radicals, the coupling product was still formed in high yields. In a reaction related to the Ullmann biaryl synthesis[17,18,19] organocoppers couple with organic halides.[20,21,22] For exemple, pentafluorobenzene couples with iodobenzene (87%), 1-bromoadamantane (93 %), methyliodide (39 %).

The present studies are directed toward the synthesis of polyfluorobicycloolefins and a study of the chemistry(1) related to these compounds.

Results and Discussion

The synthesis of 2, 2′-dichloro-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (II) from 1-iodo-2-chlorotetrafluorocyclobutene(23) (I) was accomplished by a modified Ullmann reaction. I was passed through the pyrex tube packed with copper turnings and powdered copper at 200–220° C. to yield II in 70 % yield.

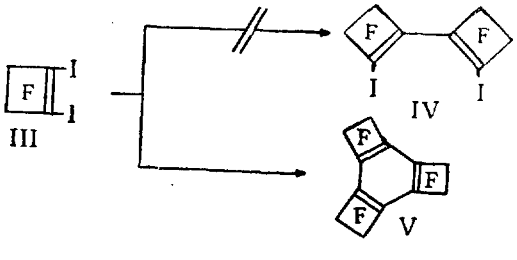


I

II

Infrared spectrum showed sharp absorption at 1575 cm^{-1} which could be assigned to a conjugated diene. The mass spectrum of II confirmed the molecular ion at m/e 318.

Unsuccessful attempts were made to obtain 2, 2′-diiodo-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (IV) from 1, 2-diiodotetrafluorocyclo-



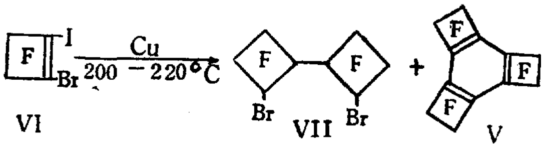
III

IV

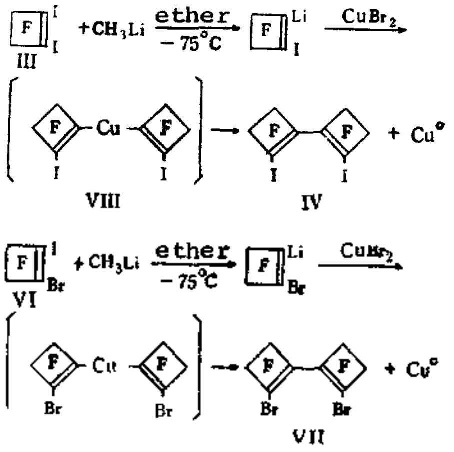
V

butene (III). When III was passed through the hot pyrex tube packed with powdered copper, tris-(di-difluoromethylene)-benzene (V) instead of IV was obtained.

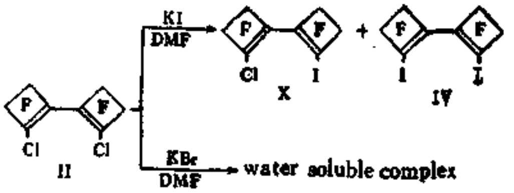
It was also found that 1-iodo-2-bromotetrafluorocyclobutene (VI) undergoes a similar reaction to give predominantly V and a very small small amount of 2, 2′-dibromo-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobutenyl (VII) which was isolated by fractional sublimation.



Compounds IV and VII were prepared in ether at −75° C. by a heterogenous reaction between the corresponding vinyllithium and cupric bromide. A solution of III or VI in anhydrous diethylether solution was cooled to −75° C. This followed by the addition of methyllithium. The reaction mixture was stirred for one hour, and cupric bromide was added. The solution turned a dark blue which indicated that presumably a copper-bridge compound as an intermediate was formed. The reaction mixture was allowed to attain room temperature after which time the solvent was removed to yield VII and IV respectively.



It was also observed that iodination of compound II with potassium iodide in DMF reacted rapidly to give a mixture of mono-and diiodo "dibox" compounds. However, bromide under similar conditions did not appear to yield compound VII but, rather a salt-like complex, which dissolved in water.

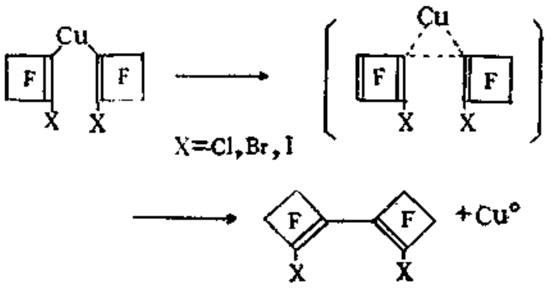


It was not possible to isolate the intermediaties of compounds VI and IV from the copper reactions. However, these reactions agreed with Kauffmann's[24] observation in the synthesis of conjugated olefins using cuprous chloride as a catalyst.

$$2\begin{matrix}R\\R'\end{matrix}\!\!>C=CHMgX\xrightarrow[\text{THF}]{2\,CuCl}2\left(\begin{matrix}R\\R'\end{matrix}\!\!>C=CHCu\right)$$

$$\xrightarrow{20^\circ}\begin{matrix}R\\R'\end{matrix}\!\!>C=CH-CH=C\!\!<\begin{matrix}R\\R'\end{matrix}+Cu^\circ+Cu^{+}$$

Though the machanism of the copper reaction reaction remains somewhat obscure, it could be postulated that compound IV and compound VII were obtained through a three-center reaction mechanism as shown below.

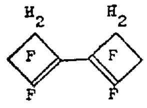
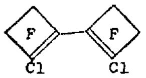
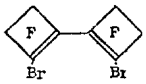
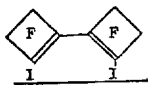


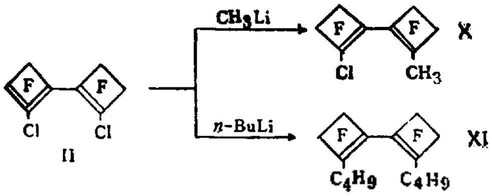
The infrared spectrum of compounds VII and IV displayed absorptions at 1550cm^{-1} and 1520 cm^{-1} respectively, which are ascribable to conjugate olefinic stretching frequencies.

Although little is known of the infrared spectra of polyfluorinated "dibox" compouds, it is interesting that the double bond stretching frequency increases from 1520 cm^{-1} to 1575 cm^{-1} on going from compounds IV to II. This is probabily due to the mass effect which is in agreement with Adam's[25] observation which indicates that the conjugate system bearing bulkier halogen substituents at the vinylic site, (though minor alternation in intensity occurs) the double bond stretching vibration moves progressively to lower frequency region. The absorption bands for the "dibox" compounds are listed in *Table* 1.

The metallation reactions between 2, 2′-dihalo-3, 3, 3′, 3′4, 4, 4′, 4′-octafluorobicyclobutenyl and alkyllithium were studied. It was found that the 2, 2′dihalo- "dibox" compounds have no tendency of undergoing lithiumhalogen interchange. This is not surprising in view of the nature of a highly reactive halogen bonded to conjugated vinylic carbon. It was observed that compound II reacts with n-butyllithium to give mainly 2, 2:-disubstituted "dibox" compounds XI. It was also found that compound II reacts simlarly with methyllithium to give exciusively mono substituted "dibox" colmpound X. This indicated that a nucleophilic reaction took place at the most susceptible sites of 2 and 2′ position.

Table 1. I. R. spectra and melting points of "Dibox" compounds

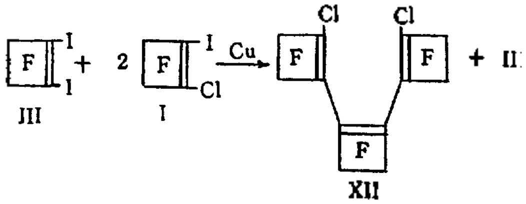
Compound	mp./C°	$\nu_{C=C}$/cm^{-1}
	50-55^{a}	1655
	68-68.5	1575
	87-88	1550
	148-148.5	1520



II X XI

The preparation of 2, 2′-dilithium "dibox" compound was also attempted. Compound VII and compound IV with methyllithium in ether at −75° C., did not yield any dilithium "dibox" compou nd but only tarry materials.

The synthesis of 3, 3, 4, 4-tetrafluoro-1, 2, di (3′, 3′, 4′, 4′-tetraflouoro-2′-chlorocyclobut-1′-enyl)-cyclobut-1-ene (XII) was achieved. The mixture of compound I and compound III (molar ratio of 2 : 1) was passed through a pyrex tube packed with powdered copper heated to 200-220° C. A mixture of compound XIII and compound II (ratio of about 4 : 1) separated compound XII by fractional sublimation. Infrared spectrum contained a sharp absorption at 1625 cm^{-1} corresponding to a conjugated triene stretching frequency.



III I XII

Further work of coupling reactions was studied with 1-iodo-2-chlorohexafluorocyclopentene XIII. Compound XIII was passed through the pyrex tube packed with copper, An unexpected tricoupled compound, tris-(tri-difiuoromethylene)-benzene (XIV) was obtained. It was also found that the polyfluorocyclopentene system also undergoes coupling reaction to give exclusively by tri-coupling product XIV.

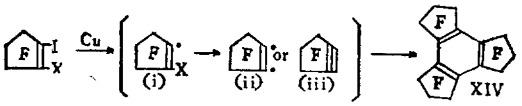
XIII XIV

X=Cl,Br,I.

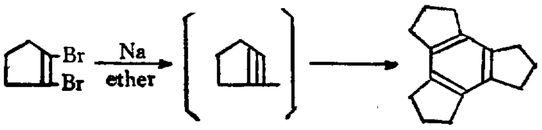
A modification of the Ullmann procedure led to improved yield. Perfluorocycloalkenyliodide was passed through a pyrex tube packed with copper turnings and powdered copper heated to about 200–220° C. Solid products were obtained in good yield and characterized by mass spectra and elemental analysis. (See experimental compounds II, V, XII and XIV.)

The exact role that copper plays is yet to be determined, although it is the only one of a large number of metals so far tested that achieves the coupling. These studies of copper-promoted reductive couplings of vinyl iodides or bromides with themselves may well follow the same mechanistic pathway as the Ullmann reaction. This reaction produces polyfluorobicycloalkenyls from polyfluorocycloalkene and copper, that is, a two-step proces, the reaction starting with an attack by copper at the vinyl iodine or bromine to form an activated complex at the metal surface. This step should be influenced by the susceptibility of the system to nucleophilic attack at halogen and is thus favered by electron withdrawing substituents. In the second step, the activated complex decays to cuprous halide and the radical species (i). With respect to this point, it is perhaps significant that there is an almost quantitative loss of iodine or bromine but not fluorine from polyfluorocycloalkenes, in the reaction with copper. This would suggest that the reactions involving copper are essentially homolytic.

It is proposed that the next step in the reaction of polyfluorocyclopentenes with copper involves formation of a hexafluorocyclopentyne (iii) or a hexafluorocyclopentene diradical (ii) by loss of the halogen atom X.



Roberts^{26} and Peters^{27} found evidence for the intervention of cyclopentyne as an intermediate in the nucleophilic substitution reaction of cyclopropenylhalide. In studies designated to determined the minimumring size for operation of the elimination-addition mechanism, they found that an entity with the symmetry properties of cyclopentyne must be involved in the formation of 1-phenylcyclopentene from 1-chlorocyclopentene from 1-chlorocyclopenten-1-C^{14} and phenyllithium. The occurrance of cyclopentyne as a reaction intermediate was previously suggested. Faborskii^{28} proposed that tris-(trimethylene)-benzene, formed by the action of sodium in ether on 1, 2-dibromocyclopentene, arose from the trimerization of cyclopentyne.



Very recently Wittig^{29} appears to have trapped cyclopentyne as a Diels-Alder adduct in similar reactions.

The preparation of 1-phenylcyclopentene-1-C^{14}

is summarized in *Fig.* 1.

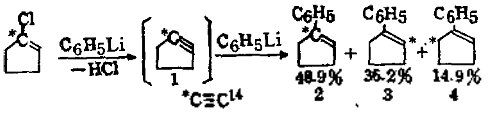
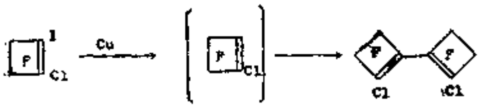


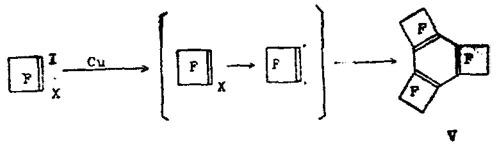
Fig. 1

Clearly, the reaction of phenyllithium with 1-chlorocyclopentene-1-C^{14} proceeds with rearrangement, and the extent of formation of 1-phenylcyclopentene-1-C^{14} is almost exactly that which would be expected for cyclopentyne (1) as an intermediate. The 14.9% 1-phenyl cyclopentene-5-C^{14} formed in the reaction most probably arises from a phenyllithium-induced allylic rearrangement of the double bond of the first-formed 1-phenylcyclopentene-2-C^{14} (3).

Similarly, the formation of compound II presumably proceeds through 2-halotetrafluorocyclobutene free radical, since it is difficult to form cyclobutyne due to the ring strain. However, from the formation of compound V, even though in very low yield (13 %), it could be speculated that 1, 2-diiodotetrafluorocyclobutene also could form a diradical to some extent as an intermediate of the coupling reaction. This agrees with the low yield (13%) of compound V in comparison to the yield (55 %) of compound XIV.



II

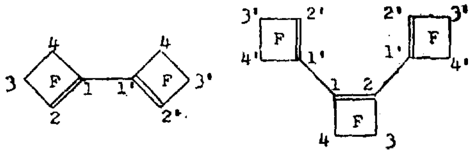


V

X=Br, I

The precise nature of these reactions remain a subject for speculation, however, it is almost certain that free radical intermediates are involved.

In the text this will be shortened slightly to permit smoother reading. Thus, bicyclobutenyl and tricyclobutenyl will be used to designate the following structure.



Experimental

Preparation of 2, 2′dichloro-3, 3, 3, 3′, 4, 4, 4, 4′-octafluorobicyclobutenyl (II) A 10g (0. 035 mol) sample of 1-iodo-2-chlorotetrafluorocyclobutene was placed in a 50 ml dropping funnel which was connected to a pyrex tube packed with copper turnings and 20 g of powdered copper. As shown in *Fig.* 2, the 1-iodo-2-chlorotetrafluorocyclobutene was passed through (one drop per 7 seconds) the pyrex tube (or with a dry nitrogen stream) slowly at 200-220° C. (external temperature). The crude solid product thus obtained was recrystallization from n-hexane followed by sublimation to yield 3. 9 g (71 % of theory) 2, 2′-dichloro-3, 3, 3′, 3′, 4, 4, 4:, 4:-octafluorobicyclobutenyl (II). m. p. 68-68. 5° C.

Anal: Calcd. for $C_8Cl_2F_8$: C, 30. 3: Cl, 22. 2: F, 47. 7.

Found: C, 29. 84, Cl, 21. 97: F, 47. 88.

The infrared spectrum for compound II contained a strong absorption at 1575 cm^{-1} corresponding to the conjugated olefinic stretching frequeuency. The mass spectrum of II exhibits a peak corresponding molecular ion at m/e—318.

Preparation of 2, 2′-diiodo-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (IV) A solution of 9. 5 g (0. 025 mol) of 1, 2-diiodotrafluorocyclobutene in a 90 ml of anhydrous diethyl ether contained in the previously described reaction

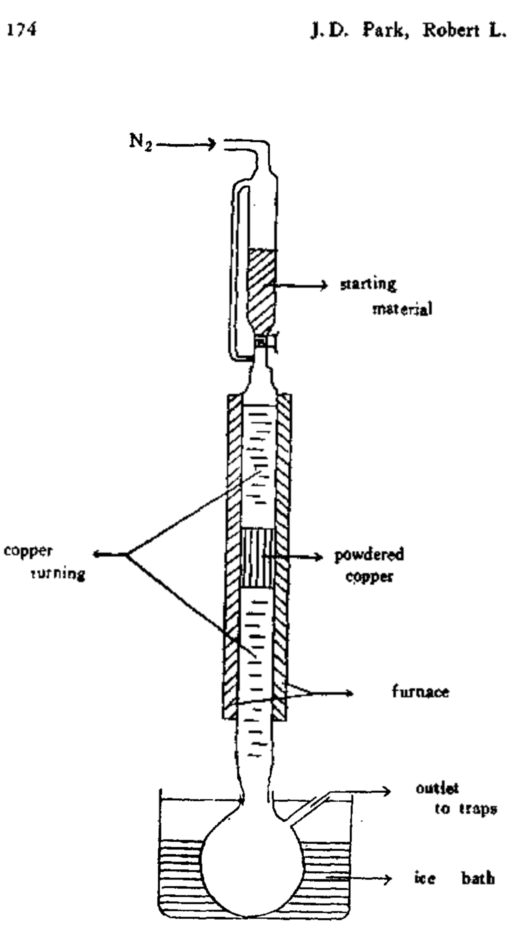


Fig. 2 Apparatus for Coupling Reaction

vessel was cooled to -75° C. Methyllithium (11.3 ml of 2.26*M* in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes and the temperature was not allowed to rise over -65° C. After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at −75° C, and 3 g (0.0124 mol) of cupric bromide subsequently added. After the reaction mixture was stirred for an additional 30 minutes, it was allowed to reach gradually to room temperature. The organic layer was separated and the solvent was removed in a rotary evaporator. The crude solid product was rcerystallized from *n*-hexane followed by sublimation to yield 2.9g (23% of theory) of 2, 2′-diiodo-3, 3, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (IV). m. p. 148.0–148.5° C.

Anal: Calcd. for $C_8F_8I_2$: C, 19.1: F, 30.3: I, 50.5.

Found: C, 19.20: F, 30.67: I, 50.11.

The infrared spectrum of compound IV showed a sharp absorption at $1520\ cm^{-1}$ corresponding to an olefinic stretching frequency, and a mass spectrum gave an intense molecular ion at m/c =502.

Preparation of Tris-(di-difluoromethylene)-benzene (V) A 7.6 g (0.02 mol) of 1, 2-diiodotetrafluorocyclobutene was placed in a 50 ml dropping funnel which was connected to a pyrex tube packed with copper turnings and 20 g of powdered copper. The 1, 2-diiodotetrafluorocyclobutene was passed through the pyrex tube slowly at 200–220° C. The crude solid product thus obtained was recrystalized from *n*-hexane followed by sublimation to yield 1.0 g (40.2% yield) of tris-(di-difluoromethylene)-benzene(V). m. p. 135–136° C.

Anal: Calcd. for $C_{12}F_{12}$: C, 38.71; F, 61.29.

Found: C, 38.55; F, 61.32.

The infrared spectrum of the compound V contained a strong absorption at $1630\ cm^1$ ascribable to double bond stretching frequency and the mass spectrum confirmed the assigned structure with a molecular ion at m/e=372.

Preparation of 2, 2′-dibromo-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (VII) A solution of 8.3 g (0.025 mol) of 1-iodo-2-bromotetrafluorocyclobutene in 80 ml of anhydrous diethyl ether in a 250 ml reaction vessel equipped with two reflux condensers (the first topped with a gas inlet tube, the other with a drying tube), a magnetic stirring assembly, and a serum cap was cooled to −75°C. (dry ice acetone bath). Methyllithium (11.5 m*l* of 2.15 *M* in diethyl ether) was added in a drop-wise manner by means of a syrings. The addition took 5 minutes. The reaction mixture was stirred for an additional 50 minutes at −75° C. and subsequently, was added 3 g (0.0125 mol) of cupric bromide. After the reaction mixture was allowed to reach gradually to room temperature, the organic layer was separated and the solvent was removed in a rotary evaporator. The crude solid product was recrystallized from n-hexane followed by sublimation, to yield 2 g (29 % of theory) of 2, 2′-dibromo-3,3, 3′,3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (VII). m. p. 87–88° C.

Anal: Calcd. for $C_8Br_2F_8$: C, 23.53; Br, 39.46; F, 37.20.

Found: C, 23.90; Br, 37.27; F, 36.96.

The infrared spectrum of compound VII displayed a sharp absorption at 1550 cm^{-1} ascribable to conjugated olefinic stretching frequency. The mass spectrum gave an intense molecular ion at m/e=406.

Preparation of 2-chloro-2′-methyl-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (X) A solution of 3.2 g (0.01 mol) of compound II in 80 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to −75° C. Methyllithium (10 ml of 2.15 *M* in diethyl ether) was added in a dropwise manner by meaner by means of a syringe. The addition took 5 minutes. After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at −75° C. and allowed to reach gradually to room temperature at which point the reaction mixture was washed with water. The organic layer was separated, dried over an anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was recrystallized from n-hexane followed by sublimation to yield 25.6 g (87 % of theory) of 2-chloro-2′-methyl-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (X). m. p. 89–90° C.

Anal: Calcd. for $C_9ClF_8H_3$: C, 36.24: Cl, 11.74: F, 51.00: H, 1.01.

Found: C, 36.05: Cl, 11.81: F, 51.21: H, 0.90.

The infrared spectrum of compound X contained sharp absorption at 1598 cm^{-1} corresponding to an olefinic stretching frequency. The mass spectrum confirmed the assigned structure with a molecular ion at m/e=298.

Preparation of 2, 2′-di-*n*-butyl-3, 3, 3′, 3,, 4, 4, 4′, 4′-octafluorobicyclobutenyl (XI) A solution of 3.2 g (0.01 mol) compound II in 80 ml of an anhydrous diethyl ether contained in the previously described reaction vessel was cooled to −75° C, n-butyllithium (9 m*l* of 2.46 *M* in THF) was added in a drop-wise manner by means of a syringe, The addition took 6 minutes. After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at −75° C. and then allowed to reach gradually to room temperature after which the reaction mixture was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent removed in a rotary evaporator. The crude solid product was sublimed to yield 2.8 g (79 % of therory) of 2, 2′-di-*n*-butyl-3, 3, 3′, 3′, 4, 4, 4′, 4′-octafluorobicyclobutenyl (XI). m. p. 28–30° C.

Anal: Calcd. for $C_{16}F_8H_{18}$: C, 53.04: F, 42.98: H, 4.97.

Found: C, 53.21: F, 42.14: H, 4.61.

The infrared sectrum of compound XI showed strong absorption at 1609cm^{-1} ascribable to double bond stretching frequency and a mass spectrum which gave an intense molecular ion at m/e=362.

Preparation of 3, 3, 4, 4-tetrafluoro-1, 2-di-(3′, 3′, 4′, 4′-tetrafluoro-2′-chlorocyclobut-1′-enyl)-Cyclobut-1-ene (XII) A mixture of 3.8 g (0.01mol) of 1, 2-diiodotetrafluorocyclobutene and 5.8 g (0.02mol) of 1-iodo-2-chlorotetrafluorocyclobutene was placed in a 50 ml dropping funnel which was connected to a pyrex tube packed with copper turnings and 20 g of powdered copper. The mixture of 1, 2-diiodotrafluorocyclobutene and 1-iodo-2-chlorotetrafluorocyclobutene was passed through (one drop per 7 seconds) the pyrex tube (or with a dry nitrogen stream) slowly at a temperature range of 200–220° C. The crude solid product thus obtained was recrystallized from n-hexane, followed by sublimation to yield 1.4 g (32 % of thery) of 3, 3, 4, 4, -tetrafluoro-1, 2-di-(3′, 3′, 4′-tetrafluoro 2′-chlorocyclobut-1′-enyl)-cyclobut-1-ene(XII). m. p. 98–99° C.

Anal: Calcd. for $C_{12}Cl_2F_{12}$: C, 32.58; Cl, 15.84; F, 51.58.

Found: C, 32.31; Cl, 15.86; F, 51.76.

The infrared spectrum of compound XII contained a sharp absorption at $1625\,cm^{-1}$ which corresponded to an olefinic stretching frequency and the mass spectrum gave an intense molecular ion at m/e=442.

Preparation of Tris-(tri-difluoromethylene)-benzene(XIII) A 8.3 g (0.03 mol) sample of 1-iodo-2-chlorohexafluorocyclopentene was placed in a 50 ml dropping funnel which was connected to a pyrex tube packed with copper turnings and 20 g of powdered copper. The 1-iodo-2-chlorohexafluorocyclopentene was passed through the copper packed pyrex tube slowly at 200–220° C. The solid product thus obtained was recrystalliyed from *n*-hexane followed by sublimation to yield 2.5 g (56 % of theory) of tris-(tri-difluoromethylene)-benzene (XIII).

Anal: Calcd. for $C_{15}F_{18}$: C, 34.48; F, 65.51,

Found: C, 34.18; F. 65.34,

The infrared spectrum of the compound XIII showed a strong absorption at $1637cm^{-1}$ ascribable to a double bond stretching frequency and the mass spectrum confirmed the assigned structure with a molecular ion at m/e=522.

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