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STEREOSELECTIVITY OF CARBENE INTERMEDIATES—V
PHENYLFLUOROCARBENE[1]

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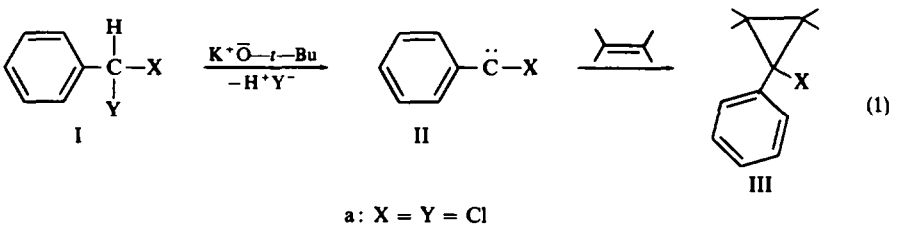
Abstract—Phenylfluorocarbene has been generated by the action of potassium t-butoxide on α-bromo-α-fluorotoluene. The carbene was added to tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, and *trans*-butene, affording in each case the anticipated 1-phenyl-1-fluorocyclopropane. Addition of the carbene to *cis*- or *trans*-butene was stereo-specific. It added to trimethylethylene so as to produce an excess of the cyclopropane isomer with the phenyl group *cis* to the greater number of methyl groups. It added to *cis*-butene with the reverse stereoselectivity. These observations are discussed. The relative rates of addition (25°) of the carbene to the enumerated olefins were: 2·7, 1·2, 1·00, 0·12, and 0·10, respectively. These results are discussed in the light of analogous data for related carbenes.

With regard to their ability to undergo base-induced alpha elimination reactions, the benzal halides may be regarded as pseudohaloforms. Thus, the classic production of dihalocarbenes from haloforms[2] finds analogy in the generation of phenylhalocarbenes from benzal halides. To date, three of the possible phenylhalocarbenes have been produced (Eq. 1). The action of potassium t-butoxide on benzal chloride (Ia) affords phenylchlorocarbene (IIa);[3] its action on benzal bromide (Ib) yields phenylbromocarbene (IIb);[4] and, as we have lately shown, its action on α-bromo-α-fluorotoluene (Ic), affords phenylfluorocarbene (IIc).[5]



I II III (1)

a: X = Y = Cl
b: X = Y = Br
c: X = F, Y = Br

With the obtention of phenylfluorocarbene,[5] we were able to extend our study of the comparative stereochemical and kinetic selectivities of the phenylhalocarbenes. The extension is described in this paper.

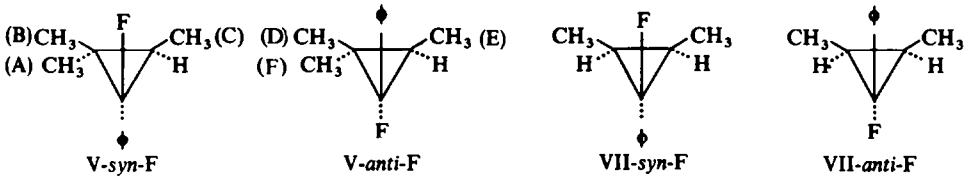
RESULTS

Syntheses of 1-*phenyl*-1-*fluorocyclopropanes.* α-Bromo-α-fluorotoluene was prepared by bromination of benzyl fluoride. Shaking this benzal halide, Ic, with an excess of potassium t-butoxide in tetramethylethylene, trimethylethylene, isobutene, *cis*-butene, and *trans*-butene led to the phenylfluorocyclopropanes, IIIc, in fair to

good yields, The new cyclopropanes were isolated and purified by distillation and/or preparative gas chromatography (gc). Pertinent data are collected in Table 1.

Structures were assigned to the new compounds on the basis of elemental analyses, IR, ^{1}H, and ^{19}F NMR spectroscopy. The proton NMR spectra of the phenylfluorocyclopropanes were very similar to those of the analogous phenylbromocyclopropanes. The latter spectra have been discussed in detail,[6] as have those of the analogous phenylchlorocyclopropanes.[7]

In the present study, addition of phenylfluorocarbene to tetramethylethylene, isobutene and *trans*-butene produced the cyclopropanes IV, VI, and VIII. NMR data for these compounds have been communicated.[5] Addition of the carbene to trimethylethylene and *cis*-butene afforded cyclopropanes V and VII, which are each mixtures of stereoisomers.



The ^{1}H NMR spectrum of the cyclopropane mixture, V, is nearly identical to that of the related phenylbromocyclopropane mixture,[6] except that (as with all the phenylfluorocyclopropanes) the methyl signals are split by coupling to the fluorine atom, J = ca. 2 c/s. Noting the shielding effect of the phenyl group on *cis* cyclopropyl methyl groups,[8] and following the arguments previously outlined,[6] one can designate the methyl absorptions of V-*syn*-F as: (A) 0·78δ, (B) and (C) ca. 1·18δ*. The absorptions of V-*anti*-F may be assigned as (D) and (E) 0·90 and 0·97δ, (F) 1·36δ. Aryl resonances were observed at 7·27 and 7·31δ. The aryl/alkyl integral ratio was satisfactory. During the course of our work, and after publication of our preliminary communication,[5] Ando and coworkers reported the synthesis of isomer mixture V.[9] Agreement of the two sets of NMR data is satisfactory.

The ^{1}H NMR spectrum of the cyclopropane mixture, VII, is again similar to that of the analogous phenylbromocyclopropane mixture. The Me groups of VII-*syn*-F appeared as a crude doublet, J = 2 c/s, at 1·18 δ. The cyclopropyl protons of this isomer absorbed in the same region. The Me protons of VII-*anti*-F appeared as a multiplet centered at ca. 0·90 δ. The cyclopropyl protons of this isomer were found at ca. 1·73 δ (broad multiplet). Aryl resonances were observed at 7·34 and 7·14 δ. Ando[9] has reported data for VII-*syn*-F which agrees with our observations.

In its ^{19}F NMR spectrum, cyclopropane mixture, V, showed two absorptions, a doublet, J = 22 c/s, at 157·7 δ, and an envelope, width at half height 10 c/s, at 188·1 δ.†

Cyclopropane mixture, VII, showed a triplet, J = 22 c/s, at 143·7 δ, and an envelope, width at half height 8 c/s, at 212·0 δ.

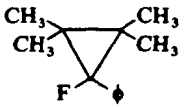
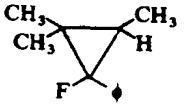
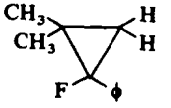
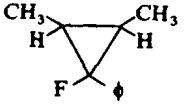
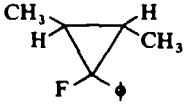
Assignment of these signals to the proper isomers is straightforward on the basis of two arguments. Firstly, *cis-vic*-H—F coupling in fluorocyclopropanes is of the order of 20 c/s, and is considerably stronger than *trans*-vic-H—F coupling.‡ Therefore,

* Relative to an internal TMS standard; CCl_4 solvent.

† Determined at 94·1 Mcps. Absorptions are reported in ppm upfield from an internal Cl_3CF standard; solvent CCl_4.

‡ See Ref. 10.

TABLE 1. 1-PHENYL-1-FLUOROCYCLOPROPANES

Cyclopropane	Olefin	Structure	B.p.[a]	Yield%[b]	Analyses Requires	Analyses Found
IV	Tetramethylethylene		73–74°/3·0 (Torr.)	81	% C = 81·20 % H = 8·91	80·70 8·93
V[c]	Trimethylethylene		75–76°/4·5	64	81·00 8·50	81·17[d] 8·40
VI	Isobutene		49–52°/3·0	74	80·45 7·98	80·08 7·83
VII[c]	*cis*-Butene		53°/1·25	58	80·45 7·98	80·32[d] 8·04
VIII	*trans*-Butene		51–58°/3·25	56	80·45 7·98	80·20 7·87

[a] Uncorrected. [b] Of crude product. [c] Mixture of isomers. [d] Analysis on the *anti*-phenyl isomer.

in both V and VII, the strongly split (low-field) absorption belongs to the *anti*-F isomers (which possesses cyclopropyl proton(s) *cis* to the fluorine atom). The envelope (high-field) absorption must belong to the *syn*-F isomer (which has no protons *cis* to the fluorine atom). Secondly, it is known that each *cis* Me group exerts a shielding effect, whereas each *trans* methyl group exerts a deshielding effect on the F atom of a fluorocyclopropane.[1,10] NMR assignments made on this basis are consistent with those made on the basis of coupling constants.

The phenylfluorocyclopropanes were thermally unstable to certain conditions. Heating of the V and VII isomer mixtures in sealed vials at 80° for 20 min. destroyed the *anti*-F isomer in each case. The *syn*-F isomers remained largely intact. Since both the analogous phenylbromo[6] and phenylchlorocyclopropanes[7] are thermally stable to harsher conditions, it is possible that the thermolyses of the phenylfluorocyclopropanes are catalyzed by traces of hydrofluoric acid. The greater stability of the V-*syn*-F and VII-*syn*-F cyclopropanes, relative to their *anti* isomers, is in accord with the expected differential intervention of steric factors if the thermolyses of these cyclopropanes proceed *via* concerted, cationic, disrotatory ring-opening reactions.[11] In this sense, the observed relative thermal stabilities of the V and VII isomers support the structural assignments made on the basis of NMR.

Despite their lability, it was possible (with care taken to avoid strong heating) to distill the phenylfluorocyclopropanes, and also to subject them to GC conditions (particularly small samples) without extensive decomposition. All of the cyclopropanes were stable for weeks at 0°. In addition, they could be resubmitted to the original preparative reaction conditions and then quantitatively recovered.

Stereospecificity. GC permitted separation of cyclopropane VIII from the mixture of cyclopropanes, VII. It was thus shown that the addition of phenylfluorocarbene to *trans*-butene produced less than 2% of the *cis*-dimethylcyclopropanes, VII; and that the addition of the carbene to *cis*-butene produced less than 2% of the *trans*-dimethylcyclopropane, VIII. The stereospecificity of the addition reaction was greater than 98%.

Stereoselectivity. The stereoselectivity of phenylfluorocarbene addition to trimethylethylene and *cis*-butene was determined by integration of the appropriate signals in the ^{19}F NMR spectra of the V and VII isomer mixtures. Only crude reaction products were employed in these determinations, and the isomer ratios observed did not change upon resubmission of the product mixtures to the reaction conditions. For the carbene addition to trimethylethylene, V-*syn*-F/V-*anti*-F was found to be 0·76 and 0·76, in separate experiments. For the carbene addition to *cis*-butene, VII-*syn*-F/VII-*anti*-F was found to be 1·23 and 1·23, in separate experiments. Corresponding data has been reported for the addition of phenylfluorocarbene, generated by the action of potassium t-butoxide on α-chloro-α-fluorotoluene at 60–80°.[9] Values of 0·76 and 2·0, respectively, were reported for the above isomer ratios.

Relative rate experiments. The various phenylfluorocyclopropanes could be separated by GC, on a SE-30 column, with minimal decomposition. Analyses of prepared mixtures allowed calibration of the thermal conductivity detector, and also demonstrated that the GC analyses accurately reflected the mixture composition.

Competition experiments, in which known mixtures of olefins were employed as carbene substrates, were carried out. A slight excess of base, and, in general, a 10-fold excess of each olefin (relative to carbene) were maintained in these reactions. The

reaction temperature was ca. 25°. GC analyses of the crude reaction products afforded the data collected in Table 2.

TABLE 2. COMPETITION OF VARIOUS OLEFIN PAIRS FOR PHENYLFLUOROCARBENE

Case	Olefin 1/Olefin 2	k_1/k_2	%a.d.[a]
1	Isobutene/Trimethylethylene	0·85	1·2
2	*trans*-Butene/Trimethylethylene	0·085	4·1
3	Trimethylethylene/Tetramethylethylene	0·43	2·1
4	*cis*-Butene/Tetramethylethylene	0·046	1·1
5	Isobutene/Tetramethylethylene	0·37	—
6	*trans*-Butene/Tetramethylethylene	0·040	—

[a] Average deviation of two experiments.

Reproducibility in cases 1–4 is satisfactory. In addition, cross-checks are possible. From cases 1 and 3, case 5 is calculated to be 0·37. From cases 2 and 3, case 6 is calculated to be 0·037. The agreement between observed and calculated values is good. In each of the cases 1–5, the crude reaction product was resubmitted to the reaction conditions, isolated and reanalyzed. No changes in product ratios were observed.

DISCUSSION

Stereoselectivity. Carbene stereoselectivity is defined as the kinetically controlled isomer distribution observed upon addition of an unsymmetrically substituted carbene to an olefin lacking both a center of symmetry and a 2-fold axis of symmetry coincident with the double bond. In addition reactions with a variety of simple alkenes, the monosubstituted carbenes, fluorocarbene,[12] chlorocarbene,[13] bromocarbene,[13] and phenylcarbene,[8] all show little or no stereoselectivity (i.e., the isomeric cyclopropanes are produced in equal quantity).* It may be surmised that these *reactive* carbenes, which also exhibit minimal ability to discriminate between different degrees of olefinic alkylation, are adding to the olefins *via* reactant-like transition states, in which the distances between carbene and olefin substituents are too great for any kind of non-bonded interactions to contribute to the stereoselectivity.

This situation is altered with disubstituted carbenes. As illustrated in Table 3, the phenylhalocarbenes each show small, but significant stereoselectivity upon addition to alkenes.

The increased stereoselective ability of the phenylhalocarbenes, as compared to the monosubstituted carbenes, parallels the greater ability of the phenylhalocarbenes to discriminate between olefins on the basis of their alkylation patterns. For example, fluorocarbene, the most selective of the monosubstituted halocarbenes adds to tetramethylethylene only 1·5 times faster than to *trans*-butene (22°),[12] while phenylbromocarbene, from the photolysis of phenylbromodiazirine, shows a selectivity factor of 17·5 (25°) in this situation.[14]† The phenylhalocarbenes may be regarded as more stabilized, less reactive, and hence more selective species than the halocarbenes or phenylcarbene. We are led to expect a "tighter", more product-like transition

* These carbenes were produced by methods likely to lead to true divalent carbon species.

† See below, for a fuller discussion of these matters.

TABLE 3. STEREOSELECTIVITY OF PHENYLHALOCARBENES, *syn*-HALO/*anti*-HALO ADDITION,[a] ca. 25°

Olefin	ϕ—$\ddot{C}$—Br	ϕ—$\ddot{C}$—Cl	ϕ—$\ddot{C}$—F[b]
Trimethylethylene	1·28[c] (1·31)[d]	1·2[e] (1·3)[f]	0·76
cis-Butene	1·35[c] (1·55)[d]	2·2[e] (2·0)[f]	1·23

[a] Unless otherwise indicated, the data is for carbenes generated as in eq. 1. [b] This work. [c] Data of reference 6. [d] This carbene was generated by photolysis of phenylbromodiazirine; see reference 14. [e] New data determined at 25°. Data determined at 60–75° may be found in reference 7. [f] Preliminary data, of Mr. Phillip Freidenreich, for generation of this carbene by photolysis of phenylchlorodiazirine.

state for their addition reactions. In this tighter transition state, there will be non-bonded interactions which give rise to the stereoselectivity phenomenon.

It is important to note that the stereoselectivity of phenylbromocarbene and of phenylchlorocarbene is not a function of the way in which we have generated the carbene. The data in Table 3 show that these carbenes exhibit very similar stereoselectivity whether produced by an α-elimination reaction of a benzal halide, or by photolysis of a phenylhalodiazirine. Assuming that this similarity would also hold for phenylfluorocarbene, comparison of the stereoselectivity of the phenylhalocarbenes with each other, and with that of the halocarbenes is permissible.

The stereoselectivity of a carbene-olefin addition reaction has been interpreted as the balance of a delicate competition of opposing forces.[8] *Syn* addition* is favored by strong electrostatic attraction of a polarizable carbene substituent and the olefinic alkyl groups (which, relative to the ground state, have become somewhat positive during the attack of the electrophilic carbene on the π bond). *Syn* addition is opposed by steric interaction between the same groups.†

Through consideration of the resultant of this competition for each carbene substituent, it might be possible to predict the stereoselectivity of addition of a disubstituted carbene. The steric demands of a phenyl group outweigh those of a

* For a monosubstituted carbene, *syn* addition is defined as the formation *mainly* of that cyclopropane with the carbene substituent *cis* to the larger number of cyclopropyl alkyl groups. In extension of this idea to disubstituted carbenes, one substituent is used as a reference point.

† See Ref. 10 and refs cited therein. Repulsive and attractive forces operating between non-bonded atoms have a common origin in the interaction of electrons. In theory, a curve, representing potential energy as a function of distance, can be drawn for the interaction of the various groups which determine stereoselectivity. At a given distance the curve would have a shallow minimum representing attractive electrostatic interactions. At shorter distances the curve would rise steeply, representing repulsion. Since a different curve would have to be drawn for every change of carbenic or olefinic substituent, and since the shape of these curves, as well as the internuclear separation of the various atoms at the transition state of the carbene-olefin reaction is now unknown, we prefer to consider stereoselectivity in the somewhat artificial terms of a "competition" of attractive and repulsive forces. This method seems easier to manipulate while seeking to rationalize the data.

halogen atom. On steric grounds alone, therefore, phenylhalocarbenes are expected to add in the halo-*syn* (phenyl-*anti*) mode. That this is generally the case (Table 3), indicates, at least, that the attractive interactions between the phenyl group and the olefinic alkyl groups do not outweigh the similar interactions between the halogen atoms and the olefinic alkyl groups by a margin sufficient to offset the steric factors favoring halo-*syn* addition. Comparison of the stereoselectivity of phenylbromocarbene with that of phenylchlorocarbene shows only a small effect of the halogen variation. The *cis*-butene data have been interpreted to suggest that the greater polarizability of bromine, relative to chlorine, is more than offset by bromine's greater steric demands, so that, in fact, halo-*syn* addition is more pronounced with phenylchlorocarbene than with phenylbromocarbene.[6] The trimethylethylene substrate, however, shows essentially no response to the Br–Cl variation.

There is one striking point in Table 3; the novel reversal of stereoselectivity observed in the addition of phenylfluorocarbene to trimethylethylene.* This result might have been anticipated. Fluorine is the least polarizable of the halogens, and its attractive interactions with *syn* olefinic alkyl groups, during a fluorocarbene addition reaction, should be minimal. Thus, despite fluorine's small size and low steric demand, predominant fluoro-*syn* addition is *not* observed with either chlorofluorocarbene[1,10] or bromofluorocarbene.[15] Chloro- or bromo-*syn* addition is observed in these cases, and the greater polarizability of the heavier halogen atoms is presumably a more important factor than the small size of the F atom in determining the stereoselectivity. Moreover, in the reaction of either chlorofluorocarbene[1,10] or bromofluorocarbene[15] with trimethylethylene, the fluoro-*anti* addition mode is favored to a *greater extent* than is the phenyl-*anti* addition mode in the reactions of phenylbromocarbene or phenylchlorocarbene with the same olefin. Preferential fluoro-*anti* addition of phenylfluorocarbene to trimethylethylene is therefore expected, and points to the dominance of attractive electrostatic effects in determining the stereoselectivity of this reaction.

The above arguments would predict dominant phenyl-*syn* addition of phenylfluorocarbene to *cis*-butene. However, the reaction leads mainly to fluoro-*syn* product. One explanation notes that *cis*-butene is a poorer carbene acceptor than trimethylethylene (see below), and that the addition to it of phenylfluorocarbene should proceed through a tighter transition state than that involved in the trimethylethylene case. In this tighter transition state, the adverse steric factors associated with phenyl-*syn* addition may play the decisive role. A similar increased importance of steric effects in carbene additions to poor acceptor olefins has been previously noted.[1,16,17]

Discrimination. The olefin selectivity of phenylfluorocarbene (Table 2) can be normalized to an isobutene standard. The resulting data is presented in Table 4 and contrasted to the analogous phenylbromocarbene data.

It is well known that halogen substituents profoundly alter the ability of a carbene to discriminate between olefins of different substitution patterns. For example, with the olefin-pair, tetramethylethylene-*trans*-butene, singlet methylene affords a rate ratio of 1·56,[18] while dichlorocarbene yields a value of 43.[1] This increased selectivity

* A similar observation has been reported by Ando *et al.*; see Ref. 9.

has been associated with a resonance stabilization[2] of the singlet dihalocarbene, which can be represented as:

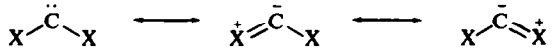


TABLE 4.

RELATIVE ADDITION RATES OF PHENYLHALOCARBENES, ca. 25°[a]

Olefin	ϕ—Ċ—Br[b]	ϕ—Ċ—F[c]
Tetramethylethylene	1·6	2·7
Trimethylethylene	1·3[d]	1·2[d]
Isobutene	1·0	1·0
cis-Butene	0·29[d]	0·12[d]
trans-Butene	0·15	0·10

[a] The carbenes were produced as per Eq. 1. [b] Data of Ref. 6. Relative addition rates for photolytically generated phenylbromocarbene can be found in reference 14. [c] This work. [d] Composite of both isomers.

This stabilization, and presumably, the selectivity of the carbene is expected to lie in the order, F > Br > Cl > I.[2] In this sense, the data of Table 4 are consistent with expectation, since phenylfluorocarbene is seen to be somewhat more selective than phenylbromocarbene. The maximum rate ratio, tetramethylethylene/*trans*-butene, is 27·0 for the fluorocarbene, and 10·7 for the bromocarbene.*

A general examination of available carbene selectivity data highlights two interesting trends. The substitution of a halogen atom for a hydrogen atom of methylene, yielding a *monohalocarbene*, leads to only a small enhancement in olefin discrimination.† Moreover, within the monohalocarbene series, change of the halogen atom from bromine to chlorine to fluorine again leads to only a minor selectivity enhancement. Thus, over the olefin series of Table 3, the maximum rate ratios are 1·18 for bromocarbene (−30°),[13] 1·21 for chlorocarbene (−30°),[13] and 2·10 for fluorocarbene (22°).[12] On the other hand, *dichlorocarbene* exhibits a maximum rate ratio of 43 over this olefin series.[1] Not only is its selectivity far greater than that of chlorocarbene, but the effect of successive chlorine substitution in the series, methylene, chlorocarbene, and dichlorocarbene, is seen to be unequally additive. The major enhancement of selectivity comes with introduction of the *second* halogen. Furthermore, sensitivity to halogen variation is greater with the dihalocarbenes than with the monohalocarbenes. Fluorochlorocarbene (−10°) exhibits a rate ratio of 320 over the selected olefin span.[1] This is larger than the selectivity spread of dichlorocarbene (43) by a factor of 7·4, and contrasts to a similar factor of 2–3 for the comparative selectivities of fluorocarbene and chlorocarbene under similar conditions.

Interpretation of these data is difficult, but, if the carbene stabilizing effect of halogen atoms is to be mainly associated with a stabilization of the carbene's ground state,[20] then it would seem that there may be some special stabilization of the dihalocarbene molecules, not implicit in the simple resonance formulation given

* The phenylhalocarbenes add stereospecifically to *cis*- and *trans*-butene.[6,7] Their reactive states are therefore most likely to be singlet.[19]

† See above and Ref. 18.

above. The existence of this effect, and also its origin, must be considered speculative, but we feel that it is worthwhile to call attention to these emerging selectivity patterns so as to spur further experimental and theoretical investigations.

In terms of the above discussion, the phenylhalocarbenes occupy a middle position between the monohalocarbenes (or phenylcarbene) and the dihalocarbenes. Both phenylbromocarbene and phenylfluorocarbene are more selective (at 25°) than the halocarbenes or phenylcarbene (at −10°). Over the selected olefin set, the largest rate ratios are phenylbromocarbene (*via* Eq. 1) 10·7,[6] or (from phenylbromodiazirine) 17·5,[14] and phenylfluorocarbene 27·0 (Table 4). This is a substantial enhancement of selectivity, when compared to the monohalocarbenes, though still inferior to dihalocarbene selectivity.* However, the sensitivity to halogen variation in the phenylhalocarbenes appears to be small, only a factor of 2·5 for the bromine to fluorine change, when the carbenes are generated as per Eq. 1. If phenylhalocarbenes produced in this manner are actually compexed to the generative base,[14] then their innate selectivity differences may be somewhat leveled, since the carbene centers' orbitals will not be completely free to achieve maximum interaction with substituent groups. It may thus be somewhat unfair to compare the data of Table 4 with analogous data for the monohalocarbenes or phenylcarbene, which were produced by methods likely to lead to free carbenes. This is also true of comparisons with the dihalocarbenes, which, though produced by a base-induced α-elimination reaction, probably approximate to free carbenes.† A more comparable set of selectivity data for the phenylhalocarbenes should be available from a study of the photolytically produced species. Such a study has been completed for phenylbromocarbene,[14] and similar investigations of phenylchlorocarbene and phenylfluorocarbene are being pursued in this laboratory.

EXPERIMENTAL

Reagents. Benzyl fluoride was obtained from Columbia Organic Chemicals Co. The olefins and their sources were: tetramethylethylethylene, Chemical Samples Co.; trimethylethylene, Aldrich Chemical Co.; isobutene, *cis*-butene, and *trans*-butene, Matheson Co. The olefins were all rated 99% pure.

α-Bromo-α-fluorotoluene. Benzyl fluoride (10 g), N-bromosuccinimide (17 g) and CCl_4 (40 ml) were mixed in a Pyrex, round bottom flask. The flask was fitted with a reflux condenser. Its contents were stirred magnetically and irradiated, at very close range, with a G. E. PH/RFL2, "Photoflood" lamp for 1·5 hr. The product mixture was then filtered. The residue was washed with CCl_4 and the wash was combined with the original filtrate. The combined CCl_4 solns were dried over $CaCl_2$. The drying agent was filtered, and CCl_4 was removed on a rotary evaporator. The residue was distilled at 70·5–73°/9 Torr., to afford 11·7 g (68%) of α-bromo-α-fluorotoluene. The proton NMR spectrum revealed a one proton doublet centered at 7·20 δ (CCl_4, with internal TMS), J_{HF} = 50 c/s, and a five proton multiplet centered at ca. 7·25 δ. The ^{19}F NMR spectrum showed a doublet centered 130·8 ppm upfield from an internal Cl_3FC standard (CCl_4 solvent), J_{HF} = 49 c/s. (Found: Br, 42·6. Calc. for C_7H_6BrF: Br, 42·3). ‡

1-Phenyl-1-fluorocyclopropanes. All of the cyclopropanes summarized in Table 1 were synthesized by the same procedure. Cyclopropane IV, 1-phenyl-1-fluoro-2,2,3,3-tetramethylcyclopropane is presented as an example. Tetramethylethylene (14 g, 167 mmoles), α-bromo-α-fluorotoluene (2·0 g, 10·6 mmoles), and t-BuOK (MSA Research Corp., 2·0 g, 17·8 mmoles) were sealed into a ¾" by 18" Carius combustion tube, fitted with a screw-top (Teflon gasket seal).§ The tube was secured to a rotary mixer and maintained, with

* See above.

† See the brief discussion of this point in Ref. 6.

‡ All microanalyses were by Micro-Tech Laboratory, Skokie, Ill.

§ For low-boiling olefins, the Carius tube was charged and sealed at −70°, then warmed to room temp.

end-over-end mixing, for 3 days. After this time, the contents of the tube were diluted with ether and hydrolyzed with ca. 50 ml water. The organic phase was washed twice with its own volume of water, and then dried over $CaCl_2$. Removal of the drying agent and stripping of the low-boiling organic material afforded 2·0 g of a yellow oil. GC (20%SE-30 column, 5 ft, ¼", 148°) indicated that the desired product, IV, constituted about 80% of this oil. IV was purified either by preparative GC, or by distillation over a small column at 73–74°/3 Torr.

Yields, b.ps, and analyses for the new phenylfluorocyclopropanes appear in Table 1. NMR data (^1H and ^{19}F) appear in Ref. 5, and in the "Results" section, above.

Competition experiments. Olefin A and olefin B were placed in a 6" Carius tube at −70°. α-Bromo-α-fluorotoluene (1·0 g, 5·3 mmoles) and t-BuOK (1·0 g, 8·9 mmoles) were added. The tube was sealed, warmed to room temp, and secured to the rotary mixer for 3 days. After this time, the tube was cooled to −70° and opened. The contents were washed twice with 20 ml portions of water and once with 20 ml sat $NaHCO_3$ aq. After drying ($CaCl_2$), excess olefin was removed on a rotary evaporator. The crude product mixtures were analyzed by GC on the SE-30 column (105°). Requisite peak areas were provided by a recorder fitted with a Disc Integrator. Relative rates were calculated from product ratios (corrected for relative detector response) by means of the standard expression $k_1/k_2 = P_1/P_2 \times O_2/O_1$, where the P_i quotient represents the cyclopropane product ratio, and the O_i quotient represents the mole ratio of starting olefins. Results of these experiments appear in Table 2. Relevant control experiments are described above.

Phenylchlorocarbene experiments. The data for the phenylchlorocarbene addition reactions, described in Table 3, were obtained from experiments and NMR analyses carried out as described, in detail, in Ref 7 (benzal chloride studies), except that the reactions were carried out at 25°, with t-BuOK obtained from Alpha Inorganics Co., and for a period of 3 days. The phenylchlorodiazirine studies, summarized in Table 3, made use of the experimental procedure of Ref. 14 and the analytical procedures of Ref. 7. Phenylchlorodiazirine was prepared as described in the literature.[21]

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