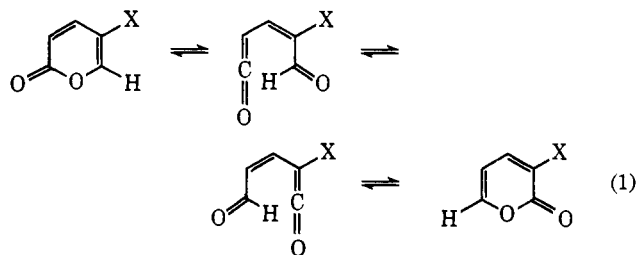


spectrometric analysis agrees closely with the nmr analysis concerning the amount of unlabeled 2-pyrone present and, importantly, demonstrates that less (<4%) doubly deuterated 2-pyrone is present than might be expected if an intermolecular protonation-deprotonation sequence were responsible for the label scrambling.

Both of the preceding "migration" reactions have accompanied decarboxylation, an exothermic process which might conceivably supply activation energy for an otherwise rare rearrangement. To test this hypothesis, 5-bromo-2-pyrone (7) was sublimed (1.0 Torr) through a glass helices packed Vycor tube maintained at 530°. Nmr and glpc analysis shows the recovered material to consist of a 54:46 mixture of 3-bromo-2-pyrone (8) and 5-bromo-2-pyrone (7). Similar pyrolysis of 8 affords a 57:43 mixture of the two isomers.<sup>7</sup>

The previous rearrangements may be rationalized by invoking initial decarboxylation (where relevant) followed by reversible electrocyclic ring opening of the pyrones to ketene aldehydes which undergo reversible 1,5-sigmatropic shifts of the aldehydic protons (see eq 1).



When the "migrating" substituent is deuterium, the sigmatropic shift is degenerate and essentially equal amounts of the 3-*d*<sub>1</sub> and 5-*d*<sub>1</sub> pyrones are present at equilibrium. If the substituent is such that the shift is not degenerate, the position of equilibrium may favor one of the two possible products. This would appear to be the case in the rearrangement of 5-methyl-2-pyrone after its (presumed) formation by decarboxylation of 1.

The ketene aldehyde postulated here as an intermediate has, in all probability, been directly observed<sup>6</sup> by low-temperature infrared spectroscopy. Irradiation of 2-pyrone in a 2:1 methylene chloride-tetrahydrofuran glass at -190° gives rise to absorption at 4.70 μ which disappears if the glass is allowed to warm to -80°. The ketene aldehyde responsible for the absorption may be trapped with methanol. Since this photochemically generated ketene is formed from a singlet excited state,<sup>8</sup> it may be that internal conversion simply affords vibrationally excited 2-pyrone which can undergo the ring-opening reaction. Hence, the photochemical and pyrolytic ring openings may be closely related. However, the 1,5-sigmatropic shift does not follow the photochemically induced ring opening,<sup>6</sup> presumably owing to a lack of activation energy. The requisite activation energy apparently can be acquired at ~500° and the sigmatropic shift consequently follows the pyrolytic ring-opening reaction.

DeJongh,<sup>9</sup> endeavoring to establish correlations between the behavior of organic molecules upon pyrolysis

(7) Identifications were made by melting point and nmr spectroscopy. See W. H. Pirkle and M. Dines, *J. Org. Chem.*, **34**, 2239 (1969).

(8) W. H. Pirkle and L. H. McKendry, *Tetrahedron Lett.*, 5279 (1968).

(9) D. A. Brant, J. D. Hribar, and D. C. DeJongh, *J. Org. Chem.*, **35**, 135 (1970).

and upon electron impact, has recently commented on the fact that pyrolytic decarbonylation of 2-pyrone at 900° affords furan while the decarbonylation of the 2-pyrone molecular radical cation affords a C<sub>4</sub>H<sub>4</sub>O radical cation reported<sup>10</sup> not to be furan-like. Since the present work makes it clear that 2-pyrones undergo ring opening at high temperatures, it is interesting to speculate whether DeJongh's pyrolytic decarbonylation occurs directly from 2-pyrone or from the ring-opened ketene aldehyde 9. Decarbonylation of the ketene may afford furan, perhaps *via* the intermediacy of a carbene.

One may also speculate as to whether 2-pyrones undergo the ring-opening and 1,5-hydrogen shift reactions on electron impact. Without asserting this to be so, we point out that this type of behavior would cause scrambling of deuterium between the 3 and 5 positions of 2-pyrone but maintain the uniqueness of deuterium in either the 4 or the 6 position. This is the experimentally observed result.<sup>10</sup>

**Acknowledgment.** This work was supported by an unrestricted Du Pont Young Faculty Grant.

(10) W. H. Pirkle and M. Dines, *J. Amer. Chem. Soc.*, **90**, 2318 (1968).

(11) Alfred P. Sloan Foundation Research Fellow, 1970-1972; to whom correspondence should be addressed.

W. H. Pirkle,<sup>11</sup> H. Seto, W. V. Turner

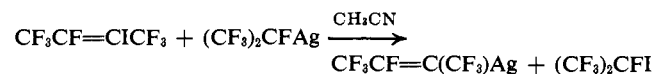
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Received July 20, 1970

## Perfluorophenylsilver<sup>1</sup>

Sir:

We wish to report the preparation of perfluorophenylsilver, the first example of a perfluorinated aromatic silver compound,<sup>2</sup> (1) from perfluorophenyl-lithium and silver trifluoroacetate, and (2) from perfluorophenyl bromide and perfluoroisopropylsilver.<sup>5,6</sup>



Halogen-metal exchange, reaction 2,<sup>6</sup> does not appear to have been observed previously with an organosilver compound.



Perfluorophenylsilver is much more stable than phenylsilver, which decomposes at about -18°,<sup>8</sup> and

(1) Presented in part at the 5th International Symposium on Fluorine Chemistry, Moscow, July 1969; Abstracts of Papers, p 85.

(2) Recently, Smith and Massey have reported the preparation of lithium bis(pentafluorophenyl)silver, mp 68-74°, from C<sub>6</sub>F<sub>5</sub>Li and AgCl at -78°, and stated that pentafluorophenylsilver was formed "as a white solid" by its exposure to "wet air or damp solvents."<sup>8</sup> Perfluorophenylsilver has also been postulated as an intermediate in the reaction of pentafluorophenylhydrazine and silver oxide.<sup>4</sup>

(3) V. B. Smith and A. G. Massey, *J. Organometal. Chem.*, **23**, C-9 (1970).

(4) J. M. Birchall, R. N. Hazeldine, and A. R. Parkinson, *J. Chem. Soc.*, 4966 (1962).

(5) W. T. Miller, Jr., and R. J. Burnard, *J. Amer. Chem. Soc.*, **90**, 7367 (1968).

(6) *trans*-Perfluoro-1-methylpropenylsilver<sup>7a</sup> has also been prepared by exchange with perfluoroisopropylsilver (unpublished work with R. H. Snider).

(7) (a) W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Amer. Chem. Soc.*, **91**, 6532 (1969); (b) *ibid.*, ref 16.

can be readily isolated. It resembles the perfluorovinylsilver compound, *trans*-perfluoro-1-methylpropenylsilver,<sup>7a</sup> in general properties<sup>7b</sup> and was only slowly converted into perfluorobiphenyl at 150°. It was decomposed in solution, apparently with the formation of perfluorophenyl free radicals, by heating, by light, and by reaction with oxygen and was hydrolyzed by moisture. It was shown to be a useful synthetic intermediate by a variety of reactions with metallic and nonmetallic halides in which silver halide was eliminated and the perfluorophenyl group introduced in place of halogen. It was also shown to undergo halogen-silver exchange reactions, with certain perhalo compounds.

(1) The addition of 0.05 mol of CF<sub>3</sub>COOAg dissolved in 25 ml of ether to a C<sub>6</sub>F<sub>5</sub>Li solution, prepared from 0.05 mol of *n*-C<sub>4</sub>H<sub>9</sub>Li in 30 ml of hexane and 0.05 mol of C<sub>6</sub>F<sub>5</sub>Br in 100 ml of ether,<sup>9</sup> during 20 min at -75° gave a brownish yellow solution and a colorless solid precipitate. Acetonitrile, 50 ml, was added and ~130 ml of distillate removed at -30 to -40° (0.5 mm). The resulting white crystals were separated and washed twice with 15-ml portions of CH<sub>3</sub>CN. After vacuum drying at 70° (0.1 mm), the product, 10.7 g, corresponded to a 78% yield of C<sub>6</sub>F<sub>5</sub>Ag (*Anal.* Calcd for C<sub>6</sub>F<sub>5</sub>Ag: Ag, 39.2. Found: Ag, 37.5). Treatment with excess HCl in ether gave a 95% yield of C<sub>6</sub>F<sub>5</sub>H.<sup>10</sup> Recrystallization of 5.43 g of the above product from 50 ml of CH<sub>3</sub>CN, dissolved at 55°, filtered to remove some insoluble dark solid, and cooled to -40°, gave fine needle-like crystals, presumably a CH<sub>3</sub>CN solvate, which were washed with precooled CH<sub>3</sub>CN and vacuum dried at 70° for 2 hr. The resulting 4.50 g of sand-colored powder contained 39.0% Ag. Treatment with HCl yielded 99% C<sub>6</sub>F<sub>5</sub>H.

(2) A 100-ml glass ampoule was charged with 0.05 mol each of C<sub>6</sub>F<sub>5</sub>Br, CF<sub>3</sub>CF=CF<sub>2</sub>, and AgF and 50 ml of CH<sub>3</sub>CN and shaken at ~25° for 60 hr. The resulting clear brown solution was filtered to remove a small quantity of black sediment and cooled to -40° to yield, after vacuum drying, 8.9 g of colorless crystals which corresponded to 65% C<sub>6</sub>F<sub>5</sub>Ag (*Anal.* Calcd for C<sub>6</sub>F<sub>5</sub>Ag: Ag, 39.2. Found: Ag, 39.1). A 97% yield of C<sub>6</sub>F<sub>5</sub>H was found after treatment with HCl. The exchange reaction appeared to be nearly quantitative, since under the experimental conditions utilized ~70% yields of (CF<sub>3</sub>)<sub>2</sub>CFAg were formed.

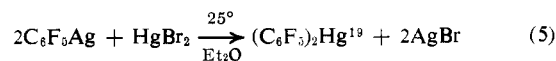
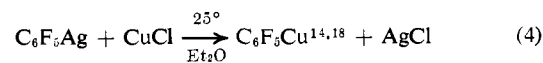
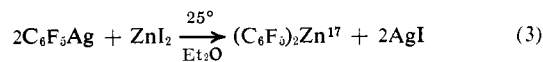
All experiments with C<sub>6</sub>F<sub>5</sub>Ag were carried out under nitrogen. Volatile products were separated and determined by glpc. After isolation and characterization, the reaction products were identified by comparison with the properties given in the references cited.

Perfluorophenylsilver dissolved in ethyl ether, acetonitrile, benzonitrile, nitrobenzene, dimethylformamide, and pyridine. It was qualitatively insoluble in benzene and hexane and formed sparingly soluble solid precipitates with tetrahydrofuran and dioxane. At room temperature in diffuse light its solutions slowly darkened and deposited solid precipitates, usually with the formation of silver mirrors. On the other hand, the crystal-

line C<sub>6</sub>F<sub>5</sub>Ag was much less sensitive. It was stored unchanged for long periods in the dark at -25° and could be handled in air for short periods without appreciable decomposition. Its properties were: mol wt (cryoscopic in nitrobenzene)<sup>11</sup> 567 (calcd for (C<sub>6</sub>F<sub>5</sub>Ag)<sub>2</sub> 550); ir (KBr, immediate obsd) 1672 (w), 1630 (m), 1602 (w), 1530 (m), 1550 (s), 1428 (s), 1380 (w), 1336 (m), 1258 (m), 1200 (w), 1182 (w), 1138 (w), 1122 (w), 1072 (s), 1052 (s), 1012 (w), 950 (s), 838 (w), 792 (w), 748 (m), and 718 (w); <sup>19</sup>F nmr (Et<sub>2</sub>O) 102.4 (*o*-F), 149.8 (*p*-F), and 161.4 (*m*-F) ppm upfield from external CFCl<sub>3</sub>. The deshielding effect of the silver atom in C<sub>6</sub>F<sub>5</sub>Ag upon the ortho fluorines was unusually large.<sup>12</sup> In a capillary melting point tube some darkening was observed up to ~240°; from ~240 to 270° a slight metallic sublimate formed; at 270-275° rapid decomposition occurred to yield a white silver deposit.

Low yields of sublimed C<sub>6</sub>F<sub>5</sub>Ag were obtained at 220° (0.04 mm) after 7 hr in addition to silver metal and perfluorobiphenyl. After 5 hr at 220° a 90% yield of C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub><sup>13</sup> was isolated from 2.8 mmol of C<sub>6</sub>F<sub>5</sub>Ag, together with metallic silver and 5% C<sub>6</sub>F<sub>5</sub>H, presumably formed from residual solvent. Under the same conditions with added Et<sub>2</sub>O, 82% C<sub>6</sub>F<sub>5</sub>H and 7% C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> were obtained. Bubbling dry oxygen through an 2% ether solution of C<sub>6</sub>F<sub>5</sub>Ag for 2 hr at 25° yielded ~50% C<sub>6</sub>F<sub>5</sub>H together with ~1% C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> and unreacted C<sub>6</sub>F<sub>5</sub>Ag. This behavior, which suggested the intermediate formation of perfluorophenyl free radicals, was in contrast to that of perfluorophenyl-copper, which undergoes thermal and oxidative coupling reactions without solvent participation.<sup>14</sup> Phenylsilver decomposes under ether at room temperature or below to form biphenyl.<sup>8,15</sup> The addition of bromine to 5 mmol of C<sub>6</sub>F<sub>5</sub>Ag in 10 ml of ether at 0° yielded 90% C<sub>6</sub>F<sub>5</sub>Br,<sup>16</sup> 6% C<sub>6</sub>F<sub>5</sub>H, and 100% AgBr.

Reactions 3-10, in which AgX was eliminated with the formation of new carbon-carbon or carbon-metal bonds, were carried out on a 3-5-mmol scale. The reactions with metal halides proceeded most rapidly. The carbon halides and silicon halide reacted more slowly or at higher temperatures. Reaction mechanisms which involve attack by silver on halogen are consistent with our results.



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(12) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1966, p 905.

(13) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

(14) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968).

(15) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); E. Krause and B. Wendt, *Chem. Ber.*, **56**, 2064 (1923).

(16) Y. Desirant, *Bull. Soc. Chim. Belg.*, **67**, 676 (1958).

(17) P. Sartori and M. Weidenbruch, *Chem. Ber.*, **100**, 3016 (1967).

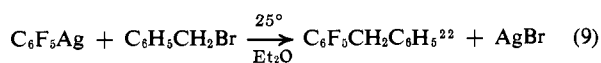
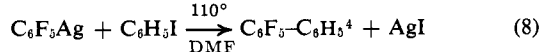
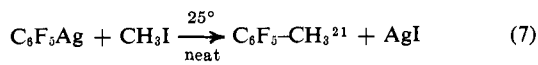
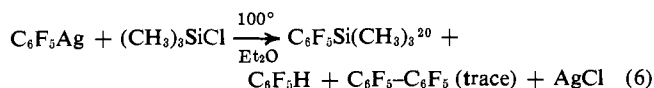
(18) We are grateful to Dr. A. Cairncross for a sample of C<sub>6</sub>F<sub>5</sub>Cu and for its ir spectrum.

(19) R. D. Chambers, G. E. Coates, J. G. Livingston, and W. K. R. Musgrave, *J. Chem. Soc.*, 4367 (1962).

(8) G. E. Coates and F. Glockling in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 448.

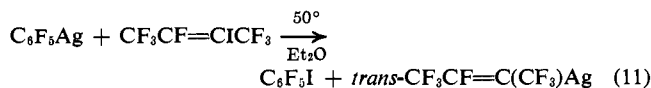
(9) P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962).

(10) R. Stephens and J. C. Tatlow, *Chem. Ind. (London)*, 821 (1957); D. Steele and D. H. Whiffen, *Tetrahedron*, **3**, 181 (1958).

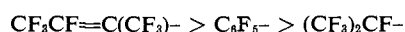


The experiments summarized in eq 3–10 demonstrate the utility of the perfluoroaromatic silver compounds as synthetic intermediates. It is believed that their use for the preparation of organometallic compounds by reaction with the corresponding halides will prove to be of particular value. The insolubility of the silver halides makes possible the preparation of compounds of elements above silver in the electromotive series as well as those below.

Perfluorophenylsilver was shown to undergo exchange with *trans*-2-iodoperfluoro-2-butene to form *trans*-perfluoro-1-methylpropenylsilver.<sup>24</sup>



Such exchange reactions are expected to yield information as to the nature of carbon–silver bonds and the electronic properties of perfluoro groups as well as to provide syntheses for new silver compounds. Our present results show that the tendency of perfluoro groups to compete for silver ion is



**Acknowledgment.** This work was supported by a grant from the National Science Foundation.

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(22) P. L. Coe, A. E. Jukes, and J. C. Tatlow, *ibid.*, **C**, 2020 (1966).

(23) A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *ibid.*, 808 (1961).

(24) Initial experiments have yielded only *trans*-1-methylpropenylsilver from both *cis*- and *trans*-2-iodoperfluoro-2-butene. These results suggest that *cis*-CF<sub>3</sub>CF=C(CF<sub>3</sub>)Ag is easily converted into its *trans* isomer.

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Received August 20, 1970

## Rotational Barriers in 1-Propyl Cations

Sir:

It is well known<sup>1</sup> that sixfold rotational barriers are generally very small. In particular, it has recently been shown<sup>2–4</sup> that the barrier in the ethyl cation is close to

(1) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

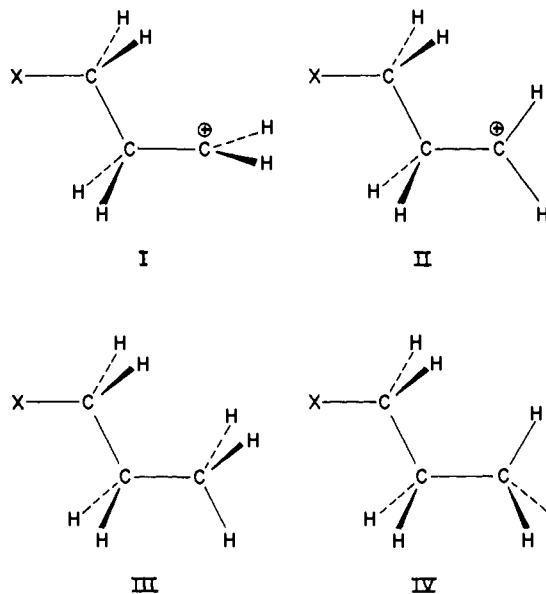
(2) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970).

(3) W. A. Lathan, W. J. Hehre, and J. A. Pople, submitted for publication.

(4) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970); *cf.* also D. T. Clark and D. M. J. Lilley, *ibid.*, 603 (1970).

zero when regular tetrahedral and trigonal bond angles are assumed and is raised only slightly (to 0.22 kcal mol<sup>-1</sup>) when distortions are allowed. The effect of a single methyl substituent<sup>3</sup> as in the 1-propyl cation (I, II, X = H) is to make the barrier twofold and raise its value to 2.2–2.5 kcal mol<sup>-1</sup>. The most stable conformation is I, which we call the *perpendicular* form, while the least stable conformation is the *eclipsed* form II.

In order to study the relative stabilizing effects of substituents X in I and II, we have performed *ab initio*



LCAO-SCF molecular orbital calculations with the STO-3G basis set<sup>6</sup> on the 1-propyl and a number of substituted 1-propyl cations. This procedure has given a reasonably satisfactory description of the rotational barriers in neutral hydrocarbons.<sup>3,7</sup> Standard values<sup>8</sup> of bond lengths and angles have been used with the additional values C<sup>+</sup>-C = 1.49 Å, C<sup>+</sup>-H = 1.12 Å as determined for the ethyl cation.<sup>3</sup> The carbonium center is taken to be trigonal.

The results of our calculations (Table I) show that the most stable conformation for all these cations is the *perpendicular* form (I). As expected, all these twofold

Table I. Total Energies (hartrees) and Potential Barriers (kcal mol<sup>-1</sup>) for Substituted 1-Propyl Cations

Substituent (X)	Energy		Barrier
	I	II	
CH <sub>3</sub>	-154.57682	-154.57088	3.73
H	-115.99294	-115.98893	2.52
F	-213.42878	-213.42542	2.11
OH	-189.81070	-189.80925	0.91
CN	-206.51636	-206.51498	0.87

barriers are larger than in the ethyl cation. A striking feature is the considerable variation of the barrier with the (distant) substituent X. This behavior is in contrast to the calculated barriers to rotation of the

(5) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970).

(6) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(7) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

(8) J. A. Pople and M. S. Gordon, *ibid.*, **89**, 4253 (1967).