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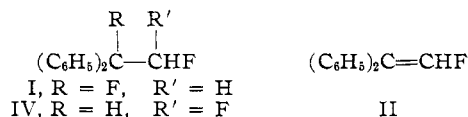
Rearrangement Accompanying the Addition of Fluorine to 1,1-Diarylethylenes<sup>1</sup>

BY JOSEPH BORNSTEIN, MARGARET R. BORDEN, FATIMA NUNES AND HARRIS I. TARLIN

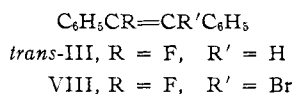
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The structures assigned by earlier investigators to the difluorides produced by the addition of fluorine to 1,1-diphenylethylene and 1,1-diphenyl-1-propene have been shown to be incorrect; actually, the isomeric rearrangement products,  $\alpha,\alpha$ -difluorobibenzyl (VI) and 1,1-difluoro-1,2-diphenylpropane (XIII), respectively, are formed. It has been found that 1,1-diphenylethylene also undergoes additive dimerization on fluorination with lead tetrafluoride to yield 1,4-difluoro-1,1,4,4-tetraphenylbutane (XIX). A possible reaction mechanism consistent with the unique structure of this heretofore undetected dimer and involving phenyl migration in a free radical intermediate is discussed.

In 1931, Dimroth and Bockemüller<sup>2</sup> reported that 1,1-diphenylethylene adds fluorine on treatment with either lead tetrafluoride or iodobenzene difluoride to yield 1,2-difluoro-1,1-diphenylethane (I). Dehydrofluorination of I with 20% ethanolic potassium hydroxide was claimed to afford 2-fluoro-1,1-diphenylethylene (II). Recently, in connection with studies on synergism of DDT, we described<sup>3</sup> an unambiguous synthesis of II and it was noted that our preparation differed markedly in properties from the compound described by the earlier investigators. At the same time attention was called to the fact that significant amounts of deoxybenzoin invariably accompanied the formation of difluoride I and it was suggested that the compound believed by Dimroth and Bockemüller to have structure II might be actually an isomer prepared by the dehydrofluorination of an unsuspected rearranged difluoride. As a result of these discrepancies the work of Dimroth and Bockemüller on the fluorination of both 1,1-diphenylethylene and 1,1-diphenyl-1-propene, the only 1,1-diarylethylenes to have been studied by them,<sup>2</sup> has been repeated. The present paper firmly establishes that these olefins add fluorine to yield rearranged difluorides and describes some experiments which offer an insight into the mechanism of this novel rearrangement.



**Fluorination of 1,1-Diphenylethylene.**—The fluorination of 1,1-diphenylethylene was effected in chloroform at 0° with lead tetrafluoride. Elemental analysis and melting point indicated that the resulting difluoride, obtained consistently in yields of 26–30%, was identical with the compound obtained earlier by Dimroth and Bockemüller,<sup>2a</sup> who reported a 42% yield.<sup>4</sup> Dehydrofluorination of this difluoride by the procedure described by these investigators yielded an olefin, which the following chemical and spectral evidence shows is actually *trans*- $\alpha$ -fluorostilbene (III) and not 2-fluoro-1,1-diphenylethylene (II) as they have claimed.



(1) Presented in part at the First International Symposium on Fluorine Chemistry, July 14–17, 1959, Birmingham, England. Two preliminary communications on this work have appeared: J. Bornstein and M. R. Borden, *Chem. Ind. (London)*, 441 (1958); J. Bornstein, *ibid.*, 1193 (1959).

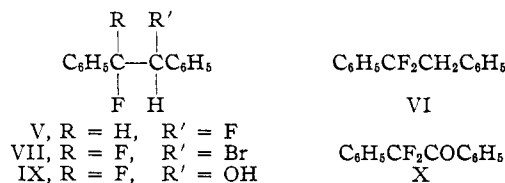
(2) (a) O. Dimroth and W. Bockemüller, *Ber.*, **64**, 516 (1931); (b) W. Bockemüller, *ibid.*, **64**, 522 (1931).

(3) J. Bornstein, M. S. Blum and J. J. Pratt, Jr., *J. Org. Chem.*, **22**, 1210 (1957).

(4) Contrary to an earlier report by A. L. Henne and T. P. Waalkes, *J. Am. Chem. Soc.*, **67**, 1639 (1945), we experienced no difficulty in carrying out this reaction in more than 20 attempts. Higher yields of the difluoride were obtained when iodobenzene difluoride was used as the fluorinating agent, as noted by Bockemüller.<sup>2b</sup>

The compound exhibited an intense band in the infrared at 6.04  $\mu$ , attributable to  $>\text{C}=\text{F}$ — conjugated with an aromatic ring,<sup>3,5</sup> and its ultraviolet spectrum was strikingly similar to that of *trans*-stilbene (cf. Experimental section). The fluorostilbene III gave a yellow-orange coloration with tetranitromethane, afforded *trans*- $\alpha$ -fluorostilbene dibromide on treatment with bromine in carbon tetrachloride, and was transformed into deoxybenzoin on solution in concentrated sulfuric acid followed by dilution with water. Oxidation of III with chromium trioxide in aqueous acetic acid gave two moles of benzoic acid in 68% yield. Hydrogenation of an ethanolic solution of III with 10% palladium-charcoal in the presence of calcium carbonate produced bibenzyl in 48% yield. Finally, and of particular interest, treatment of III with a solution of hydrogen fluoride in chloroform at 0° for two hours re-formed the precursor difluoride in 26% yield.

Since it was obvious from the proof of structure of compound III that no fluorine was present in the benzenoid rings, the difluoride derived from 1,1-diphenylethylene could be any one of the four isomers represented by formulas I, IV, V and VI. Structure IV was dismissed immediately since it is a known compound<sup>8</sup>



and yields II on boiling with 2% ethanolic potassium hydroxide. Structure I, by an  $\alpha$ -elimination reaction involving rearrangement, as well as structures V and VI could account for the formation of the fluorostilbene III on treatment with strong ethanolic potassium hydroxide. Structure I was eliminated as a possible candidate by synthesis. Thus, an authentic sample of 1,2-difluoro-1,1-diphenylethane (I) was prepared in 75% yield by stirring a suspension of 2-fluoro-1,1-diphenylethanol<sup>6</sup> in liquid hydrogen fluoride at  $-78^\circ$  for one minute. Compound I is a white solid, m.p.  $41.8$ – $42.6^\circ$ , and loses hydrogen fluoride when heated at  $96^\circ$  to give 2-fluoro-1,1-diphenylethylene (II). In contrast, the difluoride of Dimroth and Bockemüller<sup>2a</sup> is considerably more stable to heat and has m.p.  $65.5$ – $65.8^\circ$ . The following evidence proves conclusively that their difluoride is a product of rearrangement and should be formulated as  $\alpha,\alpha$ -difluorobibenzyl (VI).

Hydrogenolysis of an ethanolic solution of the difluoride with 10% palladium-charcoal in the presence of calcium carbonate gave a 41% yield of purified bibenzyl. Heating of the compound with mercuric chloride at  $170^\circ$  afforded *trans*- $\alpha$ -fluorostilbene (III) and hydrogen fluoride. The difluoride dissolved readily in

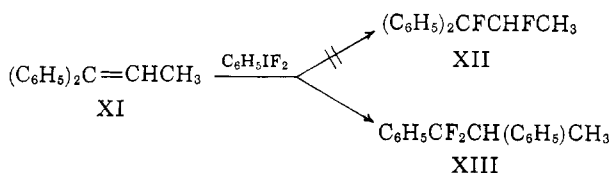
(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 41.

(6) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958).

concentrated sulfuric acid with evolution of hydrogen fluoride and the resulting green solution gave deoxybenzoin in 64% yield on dilution with water. When the fluorine addition product was treated with N-bromosuccinimide, a 64% yield of 1-bromo-2,2-difluoro-1,2-diphenylethane (VII) was realized which was dehalogenated by zinc dust in ethanol to the stilbene III in 74% yield. The bromide VII was transformed by heating with potassium hydroxide in ethylene glycol into  $\alpha$ -bromo- $\alpha'$ -fluorostilbene (VIII) in 80% yield. The infrared spectrum of VIII showed the expected absorption at  $6.08 \mu$  for conjugated  $>C=C<$  and its ultraviolet spectrum suggested a *cis*-stilbene configuration. The stilbene VIII gave an orange color with tetranitromethane, slowly decolorized bromine in carbon tetrachloride and afforded two moles of benzoic acid in 95% yield on oxidation with chromium trioxide in aqueous acetic acid.

Bromide VII, when heated under reflux with potassium acetate in dimethylformamide, gave an acetate (infrared band at  $5.72 \mu$ ) which was saponified in the crude state by hot 3% ethanolic potassium hydroxide to 2,2-difluoro-1,2-diphenylethanol (IX) in over-all yield of 77%. The infrared spectrum of the fluorocarbonyl exhibited medium intense absorption at  $2.73 \mu$ , attributable to the hydroxyl group. Oxidation of IX by chromium trioxide produced the corresponding ketone,  $\alpha,\alpha$ -difluorodeoxybenzoin (X), with a strong infrared band at  $5.86 \mu$ , indicative of an aromatic ketone containing  $\alpha$ -halogen.<sup>7</sup>

**Fluorination of 1,1-Diphenyl-1-propene.**—The fluorination of 1,1-diphenyl-1-propene (XI) was performed with iodobenzene difluoride in chloroform at  $-20^\circ$  as described by Bockemüller<sup>2b</sup>; the elemental analysis and boiling point of our product, which was obtained in 65% yield, indicated that it was identical with the difluoride he had obtained earlier in 77% yield.<sup>8</sup> Our examination of this fluorine addition product leads to the conclusion that it is 1,1-difluoro-1,2-diphenylpropane (XIII) and not 1,2-difluoro-1,1-diphenylpropane (XII) as reported by Bockemüller.



Compound XIII was recovered unchanged after being heated under reflux with 20% ethanolic potassium hydroxide (three hours), 20% potassium hydroxide in ethylene glycol (six hours) and 10% ethanolic sodium ethoxide (five hours). The resistance to base displayed by this difluoride contrasts sharply with the behavior of  $\alpha,\alpha$ -difluorobibenzyl (VI) which is smoothly dehydrofluorinated under much milder conditions. Dehydrofluorination of XIII was eventually effected by heating with 40% ethanolic potassium hydroxide for 22 hours. The resulting  $\alpha$ -fluoro- $\alpha'$ -methylstilbene (XIV), obtained in a yield of 27%, exhibited a medium intense band in the infrared at  $6.03 \mu$ , indicative of  $>C=CF-$  conjugated with an aromatic ring,<sup>3,5</sup> and its ultraviolet spectrum suggested a *trans*-stilbene configuration. This compound, which was not isomerized on boiling for two hours with glacial acetic acid containing a trace of 48%

hydrobromic acid,<sup>9</sup> slowly decolorized bromine in carbon tetrachloride, rapidly reduced potassium permanganate in aqueous ethanol and afforded both benzoic acid and acetophenone on oxidation with chromium trioxide in aqueous acetic acid.

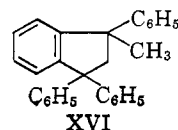
The difluoride XIII dissolved readily in concentrated sulfuric acid with evolution of hydrogen fluoride to give a red solution from which desylmethane (XV), identified by comparison with an authentic sample,<sup>10</sup> was recovered in 86% yield on dilution with water. When the difluoride was heated with a trace of mercuric chloride in air at  $190^\circ$  hydrogen fluoride was briskly evolved and a mixture of compounds XIV and XV was formed.



**Mechanism of the Rearrangement.**—The investigation of the mechanism of the rearrangement described in the present paper was carried out using lead tetrafluoride exclusively as the fluorinating agent. This reagent was prepared *in situ* by reaction of liquid hydrogen fluoride with a solution of lead tetraacetate in chloroform at  $0^\circ$  according to the procedure of Dimroth and Bockemüller, who modified the original method of Ruff.<sup>2a</sup> In connection with the fluorination of 1,1-diphenylethylene with this reagent the following three facts are significant.

First, 1,1-diphenylethylene, as reported by Dimroth and Bockemüller<sup>2a</sup> and independently confirmed by us, is resistant to lead tetraacetate in the absence of hydrogen fluoride at  $0^\circ$  in chloroform.

Second, we found that 1,1-diphenylethylene is largely dimerized by hydrogen fluoride at  $0^\circ$  in chloroform in the absence of lead tetraacetate to the well known indane XVI.<sup>11</sup> No fluorine-containing compounds are formed in this reaction.



Third, lead difluoride is always formed<sup>2a</sup> in the fluorination of 1,1-diphenylethylene with the lead tetraacetate-hydrogen fluoride system.

Our initial approach to the study of the reaction mechanism was an attempt to predict possible intermediates which might be converted to  $\alpha,\alpha$ -difluorobibenzyl (VI) when subjected to the same experimental conditions used in the preparation of VI from 1,1-diphenylethylene. This effort was totally unrewarding. The following compounds were treated with the lead tetraacetate-hydrogen fluoride reagent and none was found to yield  $\alpha,\alpha$ -difluorobibenzyl: 1. Deoxybenzoin, which always accompanies the formation of  $\alpha,\alpha$ -difluorobibenzyl, was recovered intact.

2. 2-Fluoro-1,1-diphenylethylene (II) was inert to the fluorinating agent. Compound II was of interest because it was conceivable that one of the first steps in the fluorination of 1,1-diphenylethylene is hydrogen abstraction followed by addition of a fluorine atom.

3. 1,2-Difluoro-1,1-diphenylethane (I) was partially dehydrofluorinated to the olefin II, but otherwise recovered unchanged after exposure to lead tetrafluoride. Similar results were obtained when the reaction was repeated with 1,1-diphenylethylene present.

4. 2-Fluoro-1,1-diphenyl-1-acetoxyethane (XVII) was converted to 1,2-difluoro-1,1-diphenylethane (I) in

(7) Cf. ref. 5, p. 139.

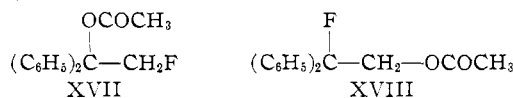
(8) Dimroth and Bockemüller, ref. 2, make no mention of having fluorinated 1,1-diphenyl-1-propene (XI) with lead tetrafluoride. For the sake of comparison, we effected the fluorination of XI with lead tetrafluoride and found that the same difluoride is produced as when iodobenzene difluoride is used. However, the product is formed in poorer yield and in a lower state of purity. The arylodiodifluoride appears to be far superior to lead tetrafluoride for this type of fluorination.

(9) D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

(10) V. Meyer and L. Oelkers, *Ber.*, **21**, 1297 (1888).

(11) E. Bergmann and H. Weiss, *Ann.*, **480**, 49 (1930).

36% yield on treatment with lead tetrafluoride. Essentially the same result was realized when the reaction was carried out with added lead difluoride. This acetate had particular appeal as a possible intermediate because it can readily be visualized as arising from the initial addition of a fluorine atom to the methylene carbon of 1,1-diphenylethylene to yield a radical which might subsequently combine with an acetoxyl radical. The isomer XVIII was considered



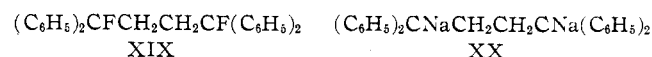
a less promising candidate because of the inertness of 1,1-diphenylethylene to lead tetraacetate and was, therefore, not investigated. Acetate XVII was prepared consistently in yields of 74% by treating the lithium alkoxide of 2-fluoro-1,1-diphenylethanol,<sup>6</sup> formed from phenyllithium and the carbinol in the cold, with acetic anhydride.

A new effort to define the reaction path was more rewarding; this consisted of an attempt to isolate intermediates by quenching the fluorination reaction. When 1,1-diphenylethylene was treated with lead tetrafluoride in chloroform at  $-40^\circ$  for ten minutes instead of at  $0^\circ$  for two hours (the usual experimental conditions), the hitherto unobserved difluoride 1,4-difluoro-1,1,4,4-tetraphenylbutane (XIX) was isolated in 20–40% yield. Dimer XIX, accompanied by  $\alpha,\alpha$ -difluorobibenzyl (VI), is also formed in somewhat lower yield at the usual temperature of  $0^\circ$  provided the reaction is quenched after ten minutes; longer reaction times lead to the complete destruction of the dimer—a fact that eliminates it as a possible intermediate in the rearrangement and probably explains the failure of the earlier investigators<sup>2</sup> to detect this compound. Indeed, when a purified sample of the dimer was treated with the lead tetraacetate–hydrogen fluoride reagent in chloroform at  $0^\circ$  for two hours, only intractable material was produced; hence 1,4-difluoro-1,1,4,4-tetraphenylbutane (XIX) cannot be a precursor of the rearranged difluoride VI. The assignment of structure XIX to the dimer is based on four facts: (1) Hydrogen fluoride was evolved from the dimer on melting; the organic residue was identified as 1,1,4,4-tetraphenyl-1,3-butadiene.<sup>12</sup>

(2) Reduction by lithium aluminum hydride in tetrahydrofuran gave 1,1,4,4-tetraphenylbutane.<sup>13</sup>

(3) Methanolysis in dioxane–sulfuric acid afforded 1,4-dimethoxy-1,1,4,4-tetraphenylbutane, identical in all respects with an authentic specimen.<sup>14</sup>

(4) Repetition of the treatment described in (2) with lithium aluminum deuteride furnished 1,4-dideuterio-1,1,4,4-tetraphenylbutane, m.p.  $121.6\text{--}122.0^\circ$ , whose infrared spectrum displayed a medium intense band at  $4.71\ \mu$ , indicative of  $\text{C--D}$  stretching. The positions of the deuterium atoms were established by comparison of its n.m.r. spectrum with that of unlabeled 1,1,4,4-tetraphenylbutane.<sup>15,16</sup>



(12) Authentic comparison sample was obtained from Pilot Chemicals, Watertown, Mass.

(13) H. Wieland and H. Kloss, *Ann.*, **470**, 215 (1929).

(14) E. Bergmann, *Ber.*, **63B**, 2593 (1930).

(15) The spectrum of the unlabeled butane shows the expected peak for the benzylic hydrogen atoms at  $6.17\ \tau$ ; this peak is absent in the deuterated compound.

(16) In view of the strong tendency of the dimer XIX to dissociate to hydrogen fluoride and 1,1,4,4-tetraphenyl-1,3-butadiene when dissolved in certain solvents, the reduction and solvolysis described above were attempted with an authentic sample of this diene; only starting compound was recovered from both attempts.

Several unsuccessful attempts were made to synthesize 1,4-difluoro-1,1,4,4-tetraphenylbutane (XIX). Thus, treatment of 1,1,4,4-tetraphenyl-1,4-butane-diol,<sup>17</sup> 1,4-dimethoxy-1,1,4,4-tetraphenylbutane,<sup>14</sup> and 2,2,5,5-tetraphenyltetrahydrofuran<sup>18</sup> with hydrogen fluoride under a variety of conditions failed to give any of the desired compound; in general, 1,1,4,4-tetraphenyl-1,3-butadiene and starting compound were recovered. Likewise, all efforts to couple 2-chloro-1-fluoro-1,1-diphenylethane (XXI) with sodium and with silver afforded none of the dimer XIX. Not unexpectedly, 1,1,4,4-tetraphenylbutane and/or 1,1-diphenylethylene were formed in these experiments. Ethane XXI was synthesized in 70% yield from hydrogen fluoride and 2-chloro-1,1-diphenylethanol<sup>6</sup> by the same procedure used to prepare 1,2-difluoro-1,1-diphenylethane (I). Compound XXI, m.p.  $52.7\text{--}53.2^\circ$ , evolved hydrogen fluoride when heated at  $110^\circ$  to give 2-chloro-1,1-diphenylethylene,<sup>19</sup> which was identical in all respects with an authentic specimen.

The isolation and characterization of dimer XIX makes it possible to speculate with some measure of confidence on the mechanism of the rearrangement. Two points should be noted. First, the rearrangement accompanying the addition of fluorine to 1,1-diarylethylenes is a unique property of fluorine. No rearrangement of the type observed with fluorine occurs when 1,1-diphenylethylene and 1,1-diphenyl-1-propene are treated with elemental bromine or with iodobenzene dichloride.<sup>2b,20,21</sup> Only normal addition products are formed<sup>22</sup> with these electrophilic halogenating agents. Second, the available evidence suggests that the fluorination of 1,1-diphenylethylene by lead tetrafluoride is a free-radical process.<sup>23</sup> Thus, the formation of the symmetrical dimer XIX is in itself an indication of the homolytic character of the reaction and in this connection it is noteworthy that this dimer is structurally identical in type with the dimer-addition product XX formed from the one-electron addition of sodium metal to 1,1-diphenylethylene.<sup>24</sup> Furthermore, it has been found recently that subjection of 1,1-diphenylethylene to partial electrochemical fluorination, a process generally considered to be free-radical in nature, also yields  $\alpha,\alpha$ -difluorobibenzyl (VI).<sup>25</sup>

If, therefore, the reasonable assumption is made that lead tetrafluoride and 1,1-diphenylethylene react by an atomic mechanism, then it must be concluded on the basis of the structure of dimer XIX that one of the first steps in the rearrangement is the generation of the unusual fluorine-containing free radical XXII. Dimerization of XXII would explain the formation of butane XIX. Isomerization of XXII to the more stable radical XXIII, followed by combination with a

(17) Obtained from Pilot Chemicals, Watertown, Mass.

(18) W. J. Wasserman and M. C. Kloetzel, *J. Am. Chem. Soc.*, **75**, 3036 (1953).

(19) W. P. Buttenberg, *Ann.*, **279**, 324 (1894).

(20) P. Lipp, *Ber.*, **56**, 567 (1923).

(21) C. Hell and H. Bauer, *ibid.*, **37**, 230 (1904); cf. J. L. Cotter, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 793 (1962).

(22) Independently verified in our laboratory.

(23) Excellent evidence already exists that the companion fluorinating agent, iodobenzene difluoride, reacts with other classes of compounds by a free-radical mechanism. Cf. ref. 2b and B. S. Garvey, Jr., L. F. Halley and C. F. H. Allen, *J. Am. Chem. Soc.*, **59**, 1827 (1937).

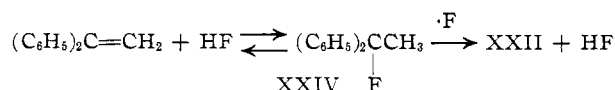
(24) C. B. Wooster, *Chem. Rev.*, **11**, 48 (1932).

(25) Private communication from Prof. H. Schmidt pointed out that the product of m.p.  $66^\circ$  prepared by the electrolytic fluorination of 1,1-diphenylethylene by H. Schmidt and H. D. Schmidt (*J. prakt. Chem.*, [4], **2**, 250 (1955)) was incorrectly formulated as 1,1-diphenyl-1,2-difluoroethane. Prompted by our earlier reports,<sup>1</sup> he has re-examined the structure of this compound and found it to be the rearranged difluoride,  $\alpha,\alpha$ -difluorobibenzyl (VI). We are indebted to Prof. Schmidt for this information. Cf. also J. Burden and J. C. Tatlow in M. Stacey, J. C. Tatlow and A. G. Sharpe, "Advances in Fluorine Chemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1960, p. 160.

fluorine atom, would account for the rearranged difluoride VI.<sup>26</sup>



It seems unlikely that radical XXII arises by the following sequence involving hydrogen abstraction.



An experiment designed to test this possibility was carried out with 1,1-diphenylethane as a model compound. No attempt was made to prepare and test 1-fluoro-1,1-diphenylethane (XXIV) itself because it would almost certainly revert to hydrogen fluoride and 1,1-diphenylethylene under the experimental conditions and thereby render the results meaningless. Treatment of 1,1-diphenylethane with lead tetrafluoride under the usual conditions yielded no evidence that hydrogen abstraction had occurred; the unchanged ethane was recovered quantitatively. This result coupled with the observation made throughout this study that the chloroform solvent is inert to the fluorinating agent suggests that free fluorine atoms are not involved in the formation of radical XXII. This view is supported by the findings of Miller and Koch,<sup>27</sup> who have demonstrated convincingly that chloroform is readily dehydrogenated to trichloromethyl radicals by fluorine atoms. It appears more likely that radical XXII is formed by transference of one fluorine atom from the fluorinating agent directly to the double bond of 1,1-diphenylethylene. Although more evidence for such a pathway would be desirable, it seems certain that the mechanism proposed recently by Bowers and his co-workers<sup>28</sup> to explain the *cis*-addition of fluorine to the olefinic bond of both pregnenolone and its corresponding acetate by lead tetrafluoride<sup>29</sup> does not apply to the 1,1-diarylethylene series. Thus, if their mechanism which involves a cyclic transition state were operating here, appreciable amounts of the normal difluoride, 1,2-difluoro-1,1-diphenylethane (I), would be produced from 1,1-diphenylethylene. Not only has compound I not been detected in our study of the fluorination of 1,1-diphenylethylene by lead tetrafluoride, but our results with I, prepared by another route (*vide supra*), indicate that had any been formed from the olefin it would have survived the experimental conditions.

Further investigations directed at clarifying the unusual direction of addition of fluorine to the double bond of 1,1-diarylethylenes and the nature of the adding species are continuing.

### Experimental<sup>30</sup>

**Fluorination of 1,1-Diphenylethylene at 0°. Formation of  $\alpha,\alpha$ -Difluorobibenzyl (VI).**—The fluorination of 1,1-diphenylethylene was performed with lead tetrafluoride in freshly purified chloroform by the procedure of Dimroth and Bockemüller<sup>2a</sup> with the following modifications: Magnetic stirring and a polyethylene reaction vessel protected by a calcium chloride drying tube were

used in carrying out the reaction; steam distillation was used to purify the concentrate of crude product. In a typical preparation using 18.0 g. (0.10 mole) of carefully purified 1,1-diphenylethylene, the forerun (800 ml.) of steam condensate contained mostly deoxybenzoin. The main fraction of distillate (2 l.), which was permeated with solid, was extracted with three 200-ml. portions of ether and the combined extracts were dried over sodium sulfate. After the ether had been removed under reduced pressure, crystallization of the solid residue from methanol separated 5.97 g. (27%) of  $\alpha,\alpha$ -difluorobibenzyl, m.p. 65.5–66.0°, as white plates. A second recrystallization from methanol afforded a sample for analysis, m.p. 65.5–65.8° (lit.<sup>2a</sup> 66°).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{12}\text{F}_2$ : C, 77.06; H, 5.50; F, 17.43; mol. wt., 218.24. Found: C, 76.9; H, 5.6; F, 18.18; mol. wt., 216 (Rast).

Column chromatography (basic aluminum oxide) of the crude reaction product failed to reveal the presence of any I or II. Only  $\alpha,\alpha$ -difluorobibenzyl, deoxybenzoin, 1,1-diphenylethylene, some resinous material and traces of an unidentified acetate (infrared bands at 5.72 and 8.15  $\mu$ ) were found.

***trans*- $\alpha$ -Fluorostilbene (III).**—Following the procedure of Dimroth and Bockemüller,<sup>2a</sup> 2.8 g. of  $\alpha,\alpha$ -difluorobibenzyl was dehydrofluorinated to 2.1 g. (82%) of *trans*- $\alpha$ -fluorostilbene, m.p. 93.5–94.0° (lit.<sup>2a</sup> 93.5°) with 22 ml. of 20% ethanolic potassium hydroxide. Recrystallization from methanol gave an analytical sample, m.p. unchanged.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{11}\text{F}$ : C, 84.84; H, 5.55; F, 9.58; mol. wt., 198.23. Found: C, 84.9; H, 5.7; F, 9.52; mol. wt., 202 (Rast).

Heating of  $\alpha,\alpha$ -difluorobibenzyl under a nitrogen atmosphere with a trace of mercuric chloride at 170° likewise afforded fluorostilbene III and hydrogen fluoride. A small amount of deoxybenzoin, which was easily removed by recrystallization from methanol, accompanied III.

In the infrared ( $\text{CCl}_4$  solution) compound III had strong absorption at 6.04  $\mu$  (conjugated  $\text{C}=\text{C}-\text{F}$ )<sup>31</sup> and its ultraviolet spectrum,  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 226 m $\mu$  ( $\epsilon$  14,650), 233 m $\mu$  ( $\epsilon$  10,480), 291 m $\mu$  ( $\epsilon$  28,200), 303 m $\mu$  ( $\epsilon$  25,980), 317 m $\mu$  ( $\epsilon$  13,340), closely resembled that of *trans*-stilbene. On irradiation of the sample solution with a GE H100-A4 mercury lamp for 5 minutes, compound III was isomerized since its ultraviolet spectrum,  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 222 m $\mu$  ( $\epsilon$  16,740), 285 m $\mu$  ( $\epsilon$  12,210), now resembled that of *cis*-stilbene. The isomeric fluoride, 2-fluoro-1,1-diphenylethylene (II),<sup>3</sup> has  $\lambda_{\text{max}}$  ( $\text{C}_6\text{H}_{12}$ ) 244 m $\mu$  ( $\epsilon$  11,850), similar to 1,1-diphenylethylene.<sup>31</sup>

***trans*- $\alpha$ -Fluorostilbene dibromide.**—To a stirred solution of *trans*- $\alpha$ -fluorostilbene (198 mg., 1.0 mmole) in 15 ml. of carbon tetrachloride was added at room temperature over a period of 10 minutes, a solution of 3 drops of bromine in 15 ml. of carbon tetrachloride. The solvent and excess bromine were removed by allowing the reaction mixture to stand in an evaporating dish overnight. The solid residue was recrystallized once from ethanol to yield 169 mg. (47.2%) of analytically pure white crystals, m.p. 168.2–168.8° dec. (bath preheated to 160°).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{F}$ : C, 47.24; H, 3.10; Br, 44.58. Found: C, 47.03; H, 3.07; Br, 44.85.

**Reaction of III with Sulfuric Acid. Formation of Deoxybenzoin.**—Compound III (25 mg., 0.13 mmole) on stirring with 3 ml. of concentrated sulfuric acid at room temperature dissolved within 15 minutes to give a light green solution. Hydrogen fluoride was evolved. After standing at room temperature for 4 hours, the solution was poured onto ice and the cream-colored solid was collected by suction filtration the following day. The product thus obtained was shown to be deoxybenzoin, m.p. 55–56°, by comparison with an authentic specimen.

**Oxidation of III.**—A 100-mg. quantity of III was heated under reflux for 3 hours with a mixture of 200 mg. of chromium trioxide, 5 ml. of glacial acetic acid, and 2 drops of water. The cooled green solution was diluted with 20 ml. of water and then extracted twice with 50-ml. portions of ether. The combined ether extracts were washed successively with water (two 10-ml. portions), 5% sodium hydroxide (two 25-ml. portions) and water (two 10-ml. portions). The dried (over sodium sulfate) extract gave no residue on removal of the ether. The combined sodium hydroxide extracts were acidified with dilute sulfuric acid and then extracted with two 50-ml. portions of ether. The combined ether extracts were washed twice with 15-ml. portions of water and dried over sodium sulfate. Removal of the solvent on the steam-bath gave 84 mg. (68%) of benzoic acid, m.p. 122–123°. A mixture melting point with an authentic sample was not depressed; both samples yielded identical infrared spectra.

**Hydrogenation of III. Formation of Bibenzyl.**—A solution of 133 mg. (0.67 mmole) of *trans*- $\alpha$ -fluorostilbene in 50 ml. of 90% ethanol, to which 100 mg. of calcium carbonate and 100 mg. of

(26) For some recent examples of free radical rearrangement reactions cf. W. B. Smith and J. D. Anderson, *J. Am. Chem. Soc.*, **82**, 656 (1960).

(27) W. T. Miller, Jr. and S. D. Koch, Jr., *ibid.*, **79**, 3084 (1957).

(28) A. Bowers, P. G. Holton, E. Denot, M. C. Loza and R. Urquiza, *ibid.*, **84**, 1050 (1962). Cf. also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 360.

(29) Prepared *in situ* from lead tetraacetate and hydrogen fluoride.

(30) Melting points are corrected and boiling points are uncorrected. Infrared measurements were made using a Baird double beam recording spectrophotometer equipped with a sodium chloride prism. Ultraviolet spectra were measured with a Cary model 11 recording spectrophotometer or with a Beckman spectrophotometer, model DU. Elemental analyses were performed by Drs. S. M. Nagy of M.I.T. and Carol K. Pitz, Needham Heights, Mass. We are indebted to Mr. Roland Gohlke, Dow Chemical Co., Framingham, Mass., for the deuterium analysis.

(31) M. Pestemer and D. Brück in Houben-Weyl, "Methoden Der Organischen Chemie," Vol. III, Part 2, 4th Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 721.

10% palladium-on-charcoal catalyst had been added, was shaken with hydrogen at an initial pressure of 38 p.s.i. at room temperature for 5 hours. After the mixture had been filtered and concentrated under reduced pressure, recrystallization of the solid residue from methanol yielded 61.2 mg. (48%) of bibenzyl, m.p. 50.5–51.5°. A mixture melting point with an authentic sample was unchanged; both specimens had identical infrared spectra.

**Addition of Hydrogen Fluoride to III. Re-formation of  $\alpha,\alpha$ -Difluorobibenzyl (VI).**—To a solution of 300 mg. (1.51 mmoles) of *trans*- $\alpha$ -fluorostilbene in 20 ml. of chloroform at 0° was added 2.0 ml. of liquid anhydrous hydrogen fluoride. The cooled reaction mixture was stirred for 2 hours and then poured onto cracked ice. The chloroform layer was separated and washed successively with water, dilute sodium bicarbonate and water. After the solution had been dried over sodium sulfate and concentrated, crystallization of the solid residue from methanol followed by sublimation (40° at 0.5 mm.) afforded 84 mg. (26%) of  $\alpha,\alpha$ -difluorobibenzyl, m.p. 64.5–66.0°. This compound was shown to be identical with the difluoride obtained from the fluorination of 1,1-diphenylethylene with lead tetrafluoride by a mixture melting point determination and infrared spectral comparison.

**Hydrogenolysis of VI. Formation of Bibenzyl.**—A solution of 513 mg. (2.59 mmoles) of  $\alpha,\alpha$ -difluorobibenzyl in 50 ml. of 90% ethanol, to which 500 mg. of calcium carbonate and 502 mg. of 10% palladium-on-charcoal catalyst had been added, was shaken with hydrogen at an initial pressure of 40 p.s.i. at room temperature for 90 hours. The mixture was filtered, concentrated and the residue was extracted with ether. After the ether extract had been washed with water and dried over sodium sulfate, the solution was evaporated to dryness under reduced pressure; the residue was crystallized from ethanol. The colorless crystals thus obtained (176 mg., 41%), m.p. 50–51°, were shown to be identical with an authentic specimen of bibenzyl by infrared spectral comparison and a mixture melting point determination.

$\alpha,\alpha$ -Difluorobibenzyl was resistant to many reducing agents. Thus, with lithium aluminum hydride in refluxing *n*-butyl ether, VI was partially converted to a mixture of bibenzyl and *trans*-stilbene; VI was recovered unchanged after exposure to 2% sodium amalgam in ethanol and to zinc dust in boiling ethanol and boiling acetic acid. Phosphorus and iodine in boiling aqueous acetic acid transformed VI to deoxybenzoin in 80% yield.

**Conversion of VI to Deoxybenzoin by Sulfuric Acid.**—Following the procedure used with *trans*- $\alpha$ -fluorostilbene, 200 mg. (0.92 mmole) of VI was converted by dissolution in 5 ml. of concentrated sulfuric acid to 115 mg. (64%) of deoxybenzoin, m.p. 55.0–55.5°, identical in all respects with an authentic sample.

**1-Bromo-2,2-difluoro-1,2-diphenylethane (VII).**—A mixture of  $\alpha,\alpha$ -difluorobibenzyl (4.58 g., 0.02 mole), *N*-bromosuccinimide (3.80 g., 0.02 mole) and benzoyl peroxide (110 mg.) in 70 ml. of freshly purified carbon tetrachloride was heated under reflux with stirring in a nitrogen atmosphere for 22 hours. The light orange-colored reaction mixture was cooled and then washed successively with water (60 ml.), 5% sodium bicarbonate (70 ml.) and water (three 50-ml. portions). After the solution had been concentrated under reduced pressure, 100 ml. of water was added to the residue and the mixture was steam distilled until 50 ml. of condensate, which contained mainly unchanged  $\alpha,\alpha$ -difluorobibenzyl (ca. 300 mg.), had been collected. The residual oil was taken up in ether and the resultant solution was washed twice with water and then dried over sodium sulfate. The solution was concentrated and the residue was distilled under reduced pressure through a semimicro column. The material boiling up to 123° (0.9 mm.) was mostly unchanged starting compound (ca. 400 mg.). The fraction, b.p. 123–127° (0.9 mm.), 4.5 g., crystallized on cooling and was recrystallized from methanol yielding 4.0 g. (64%) of 1-bromo-2,2-difluoro-1,2-diphenylethane, m.p. 44–45°.

*Anal.* Calcd. for  $C_{14}H_{11}BrF_2$ : C, 56.58; H, 3.73; Br, 26.89. Found: C, 56.6; H, 3.7; Br, 26.7.

**Dehalogenation of VII with Zinc in Ethanol. Formation of III.**—1-Bromo-2,2-difluoro-1,2-diphenylethane (207 mg., 0.70 mmole) was dissolved in 5 ml. of anhydrous ethanol. To this solution was added 200 mg. of freshly purified zinc dust and the resultant mixture was stirred and heated under reflux for 24 hours. The reaction mixture was cooled, filtered and the filtrate concentrated under reduced pressure. The residue was taken up in 50 ml. of ether and the resultant solution yielded 161 mg. of a white solid after being washed with water, dried over sodium sulfate and concentrated. Recrystallization of the solid from methanol afforded 102 mg. (74%) of *trans*- $\alpha$ -fluorostilbene, m.p. 93.5–94.0°, which was shown by a mixture melting point determination and infrared and ultraviolet spectral comparisons to be identical with the compound prepared by the action of 20% ethanolic potassium hydroxide on VI.

**$\alpha$ -Bromo- $\alpha'$ -fluorostilbene (VIII).**—1-Bromo-2,2-difluoro-1,2-diphenylethane (2.44 g., 8.2 mmoles), 35 ml. of ethylene glycol and 5.0 ml. of a solution prepared by dissolving 6.3 g. of potassium hydroxide in 3.5 ml. of water were heated together under reflux for 3.5 hours. The cloudy reaction mixture separated into two layers when cooled; the lower phase was deep brown. The

reaction mixture was extracted with two 75-ml. portions of ether and the combined extracts were washed three times with 40-ml. portions of water and dried over sodium sulfate. The solution was concentrated and the residue was distilled under reduced pressure through a semimicro column. The yield of  $\alpha$ -bromo- $\alpha'$ -fluorostilbene, b.p. 100–103° (0.3 mm.),  $n_D^{25}$  1.6267–1.6270, was 1.82 g. (80%). A sample with  $n_D^{25}$  1.6269 was analyzed.

*Anal.* Calcd. for  $C_{14}H_{10}BrF$ : C, 60.67; H, 3.64; Br, 28.83; F, 6.86. Found: C, 60.9; H, 3.6; Br, 28.6; F, 7.06.

The compound slowly crystallized on standing in the refrigerator; it had m.p. 64–65° after two recrystallizations from methanol. The stilbene gave a deep yellow color with tetranitromethane in chloroform solution and slowly decolorized bromine in carbon tetrachloride. The infrared spectrum ( $CCl_4$  solution) of the compound displayed intense absorption at 6.08  $\mu$ , characteristic of  $C=C-F$  conjugated with an aromatic ring.<sup>3,5</sup> Its ultraviolet spectrum,  $\lambda_{max}$  ( $C_6H_{12}$ ) 265  $m\mu$  ( $\epsilon$  19,230), 282  $m\mu$  ( $\epsilon$  18,840), suggested a *cis*-stilbene configuration.

Oxidation of 180 mg. of  $\alpha$ -bromo- $\alpha'$ -fluorostilbene with 350 mg. of chromium trioxide in 7 ml. of aqueous acetic acid by the procedure used with compound III afforded 151 mg. (95%) of benzoic acid, m.p. 121–122°, shown by infrared spectral comparison and a mixture melting point determination to be identical with an authentic specimen.

**2,2-Difluoro-1,2-diphenylethane (IX).**—A mixture of 329 mg. (1.10 mmoles) of 1-bromo-2,2-difluoro-1,2-diphenylethane and 200 mg. (2.04 mmoles) of finely powdered potassium acetate in 3.0 ml. of dimethylformamide containing 3 drops of methanol was heated under reflux with stirring for 48 hours. The reaction mixture was cooled to room temperature, diluted with 25 ml. of water and extracted with two 25-ml. portions of chloroform. The combined chloroform extracts were washed twice with 15-ml. portions of water and dried over sodium sulfate. Concentration of the solution under reduced pressure afforded an amber oil (strong infrared band at 5.73  $\mu$  in carbon tetrachloride solution), which was saponified without purification by heating under reflux for 1 hour with 10 ml. of 3% ethanolic potassium hydroxide. The reaction mixture was diluted with 20 ml. of water, extracted twice with 100-ml. portions of ether and the combined ether extracts were washed twice with water and dried over sodium sulfate. Removal of the solvent under reduced pressure left a cream-colored solid residue which on sublimation (60–75° at 0.5 mm.) afforded 200 mg. (77%) of 2,2-difluoro-1,2-diphenylethane, medium intense band at 2.74  $\mu$  ( $CCl_4$  solution). Crystallization from ligroin (b.p. 66–75°) yielded 127 mg. of analytically pure carbinol, m.p. 85.1–85.6°, as white, felted needles.

*Anal.* Calcd. for  $C_{14}H_{10}OF_2$ : C, 71.80; H, 5.16; F, 16.23. Found: C, 71.6; H, 5.1; F, 15.95.

**$\alpha,\alpha$ -Difluorodeoxybenzoin (X).**—A solution of 75 mg. of 2,2-difluoro-1,2-diphenylethane in 5 ml. of 70% aqueous acetic acid containing 35 mg. of chromium trioxide was allowed to stand at room temperature 17 hours. The orange solution was then heated under reflux for 30 minutes and allowed to stand at room temperature an additional 20 hours. The green solution was extracted twice with 75-ml. portions of ether and the combined colorless ether extracts were washed twice with water and dried over sodium sulfate. Concentration of the solution gave a faint straw-colored oil which, on purification by short-path distillation (90° at 0.2 mm.), yielded  $\alpha,\alpha$ -difluorodeoxybenzoin,  $n_D^{20}$  1.5527, as a colorless oil, with strong absorption in the infrared at 5.86  $\mu$  ( $CCl_4$  solution).<sup>7</sup>

*Anal.* Calcd. for  $C_{14}H_{10}OF_2$ : C, 72.40; H, 4.34. Found: C, 72.4; H, 4.5.

The 2,4-dinitrophenylhydrazone, isolated as yellow plates after one recrystallization from methanol, had m.p. 180.1–181.1°.

*Anal.* Calcd. for  $C_{20}H_{14}N_4F_2O_4$ : C, 58.25; H, 3.42; N, 13.59. Found: C, 58.40; H, 3.60; N, 13.52.

**1,2-Difluoro-1,1-diphenylethane (I).**—To 1.00 g. (4.62 mmoles) of 2-fluoro-1,1-diphenylethane<sup>6</sup> in a polyethylene test-tube cooled in a Dry Ice–acetone bath was added 0.5 ml. of liquid hydrogen fluoride. The suspension was stirred with a nickel spatula for 1 minute and then a large excess of potassium fluoride was added. The reaction vessel was removed from the cooling bath and after standing at room temperature for 15 minutes the mixture was eluted with ether. Evaporation of the resulting solution under reduced pressure at room temperature gave a white solid which was taken up in the minimum amount of methanol at room temperature. After being filtered and chilled in a Dry Ice–acetone bath the resultant solution deposited 0.760 g. (75%) of 1,2-difluoro-1,1-diphenylethane, m.p. 41.8–42.6°, as white crystals.

*Anal.* Calcd. for  $C_{14}H_{12}F_2$ : C, 77.06; H, 5.50. Found: C, 76.9; H, 5.6.

Heating of I above 96° resulted in a vigorous evolution of hydrogen fluoride; 2-fluoro-1,1-diphenylethane (II), identified by comparison of its infrared spectrum with the spectrum of an authentic sample,<sup>8</sup> was produced. Purified samples of I are stable



for many months in the refrigerator; at room temperature these samples often show signs of loss of hydrogen fluoride after two weeks. Purified I is considerably more stable than the purified analogous dibromide of Lipp.<sup>30</sup>

**Fluorination of 1,1-Diphenyl-1-propene.** Formation of 1,1-Difluoro-1,2-diphenylpropane (XIII).—Following the procedure of Bockemüller,<sup>2b</sup> fluorination of 11.0 g. (0.057 mole) of 1,1-diphenyl-1-propene<sup>32</sup> with iodobenzene difluoride<sup>33</sup> in chloroform afforded 8.6 g. (65%) of racemic 1,1-difluoro-1,2-diphenylpropane, b.p. 95–96° (1.0 mm.) (lit.<sup>2b</sup> 115–120° (2 mm.)). Redistillation through a semimicro column gave an analytical sample,  $n_D^{20}$  1.5337.

*Anal.* Calcd. for  $C_{15}H_{13}F_2$ : C, 77.56; H, 6.08. Found: C, 77.7; H, 6.0.

**$\alpha$ -Fluoro- $\alpha'$ -methylstilbene (XIV).**—To a solution of 9.0 g. of potassium hydroxide in 15 ml. of absolute ethanol was added 1.0 g. (4.32 mmoles) of 1,1-difluoro-1,2-diphenylpropane. After the resulting solution had been heated under reflux for 22 hours it was cooled and poured into a stirred mixture of ice and water to which 10.0 g. of concentrated sulfuric acid had been added. The mixture was extracted with 70 ml. of ether and the extract was washed three times with water. Concentration of the dried (over sodium sulfate) ether extract afforded a faint straw-colored oil which crystallized when scratched. The solid was taken up in methanol and after filtration and cooling of the resultant solution in the refrigerator, 0.25 g. (27%) of  $\alpha$ -fluoro- $\alpha'$ -methylstilbene separated as colorless prisms, m.p. 78.6–79.6°,  $\lambda_{max}$  (95% EtOH) 264  $\mu$  ( $\epsilon$  17,460),  $\lambda_{max}$  (CCl<sub>4</sub>) 6.03  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{13}F$ : C, 84.87; H, 6.17. Found: C, 84.65; H, 6.51.

Oxidation of 150 mg. of  $\alpha$ -fluoro- $\alpha'$ -methylstilbene was carried out with 300 mg. of chromium trioxide in 7 ml. of aqueous acetic acid by the procedure used with *trans*- $\alpha$ -fluorostilbene. Benzoic acid (121 mg.), m.p. 122.5–123.3°, was isolated and shown to be identical in all respects with an authentic sample. In addition, acetophenone was produced; it was isolated as the 2,4-dinitrophenylhydrazone (7.2 mg.). The high yield of benzoic acid (theoretical yield is 86.4 mg.) is due, without doubt, to oxidative degradation of the accompanying acetophenone. The 2,4-dinitrophenylhydrazone, after one recrystallization from glacial acetic acid, had m.p. 247–248°, and was shown to be identical with the 2,4-dinitrophenylhydrazone of an authentic sample of acetophenone by a mixture melting point determination and infrared spectral comparison.

**Conversion of 1,1-Difluoro-1,2-diphenylpropane to Desylmethane by Sulfuric Acid.**—Following the procedure used with *trans*- $\alpha$ -fluorostilbene, 900 mg. of 1,1-difluoro-1,2-diphenylpropane was converted by dissolution in 10 ml. of concentrated sulfuric acid (cherry-red solution) to 700 mg. (86%) of desylmethane, m.p. 51.5–52.0° (lit.<sup>10</sup> 53°), after one recrystallization from methanol. The substance was shown to be identical with an authentic sample<sup>30</sup> by infrared spectral comparison and a mixture melting point determination. The 2,4-dinitrophenylhydrazone had m.p. 151–152° (lit.<sup>34</sup> 150–151°) and was found to be identical in all respects with an authentic specimen.<sup>34</sup>

**2-Fluoro-1,1-diphenyl-1-acetoxyethane (XVII).**—This preparation was carried out in a nitrogen atmosphere. To a solution of 18.0 g. (83 mmoles) of 2-fluoro-1,1-diphenylethanol<sup>6</sup> in 200 ml. of anhydrous ether which had been cooled in an ice-bath for 30 minutes, was added with stirring over a 25-minute period 80 ml. of 1.16 *N* phenyllithium in ether. To the resulting white slurry was added with stirring and cooling over a 30-minute period a solution of 8.8 g. of redistilled acetic anhydride in 60 ml. of ether. The reaction mixture was then stirred successively for 1.5 hours at the ice-bath temperature, for 1.5 hours at room temperature and, finally, for 5 hours at reflux temperature. The resultant yellow suspension was then cooled in an ice-bath and treated with 100 g. of cracked ice. The ether layer was separated and washed successively with water, 10% sodium bicarbonate and water. Concentration of the dried (over sodium sulfate) extract gave an oil which was distilled under reduced pressure through a semimicro column. The fraction (18.0 g.) with b.p. 135–140° (0.5 mm.) was collected; it was a viscous, very light green oil;  $n_D^{20}$  1.5536. This substance was taken up in 100 ml. of hexane and the resultant solution was heated with Norit, filtered, and the filtrate cooled to room temperature. Seeding this solution caused 2-fluoro-1,1-diphenyl-1-acetoxyethane to separate at once as thick prisms. Refrigeration of this mixture for 8 hours afforded 16.0 g. (74%) of XVII, m.p. 51.0–51.7°;  $\lambda_{max}$  (CCl<sub>4</sub>) 5.73, 8.15  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{15}O_2F$ : C, 74.40; H, 5.86; F, 7.36. Found: C, 74.7; H, 5.9; F, 7.05.

The seed crystals used above were obtained from an early preparation of XVII by chromatography on basic alumina, which

also revealed the presence of small amounts of starting fluorocarbonyl, deoxybenzoin and 2-fluoro-1,1-diphenylethylene (II) in the crude reaction product.

Evidence that no rearrangement had occurred in the course of preparation of the acetate was obtained by heating 1.00 g. of the substance with a trace of *p*-toluenesulfonic acid at 150°. Acetic acid was evolved and 650 mg. (84%) of 2-fluoro-1,1-diphenylethylene (II) was recovered on distillation of the residue.

All attempts to effect the acetylation of 2-fluoro-1,1-diphenylethanol with acetic anhydride and a variety of acidic and basic catalysts failed. Failure was also encountered when a mixture of trifluoroacetic anhydride and acetic acid was used. Partial success was achieved with a combination of acetyl chloride and triethylamine.

**Fluorination of 1,1-Diphenylethylene at –40°. Formation of 1,4-Difluoro-1,1,4,4-tetraphenylbutane (XIX).**—In a 500-ml. heavy-walled polyethylene jar sealed with a cap holding a drying tube filled with calcium chloride, a stainless steel dial thermometer and an addition tube of polyethylene connected to a dropping funnel, were placed 12.5 g. of lead tetraacetate and 50 ml. of freshly purified chloroform. After the solution had been stirred magnetically in an ice-bath for 15 minutes the cap was removed momentarily to allow the addition of 2.2 ml. of anhydrous liquid hydrogen fluoride. The mixture was stirred an additional 30 minutes at 0° and was then cooled in a Dry Ice–ethanol bath. As soon as the temperature had dropped to –40° a solution of 4.5 g. (0.025 mole) of 1,1-diphenylethylene in 15 ml. of chloroform, precooled to 5°, was added in one portion with vigorous stirring. The temperature of the reaction mixture was maintained at –40° by intermittent application of the cooling bath. After 10 minutes the reaction was quenched by pouring the deep blue reaction mixture onto 200 g. of ice. The resultant deep brown suspension was filtered through Celite and the yellow, faintly turbid chloroform layer was separated, washed successively with water, 5% sodium bicarbonate and water and dried over sodium sulfate. Concentration of the solution under reduced pressure at 30–35° gave a cream-colored solid which was slurried with 25 ml. of cold 95% ethanol and collected by filtration; the ethanolic filtrate contained unreacted 1,1-diphenylethylene mainly, and small amounts of  $\alpha,\alpha$ -difluorobenzyl (VI) and deoxybenzoin. Recrystallization of the solid from acetone afforded analytically pure XIX (1.25 g., 25%), which gave no coloration with tetranitromethane in chloroform and was inert to cold aqueous potassium permanganate.

*Anal.* Calcd. for  $C_{26}H_{24}F_2$ : C, 84.39; H, 6.07; F, 9.54; mol. wt., 398. Found: C, 84.2; H, 6.0; F, 9.90; mol. wt., 339 (Rast).

Purified XIX is stable indefinitely at room temperature and has a sharp but variable melting point in the range 157–189°. Hydrogen fluoride is vigorously evolved when XIX melts and a light yellow residue is produced. Chromatography of this residue on neutral alumina (hexane–benzene solution), followed by one recrystallization from ethyl acetate, afforded in 75% yield 1,1,4,4-tetraphenyl-1,3-butadiene, m.p. 195.8–196.5° (lit.<sup>35</sup> 192–193°). This substance was shown to be identical with an authentic specimen<sup>12</sup> by a mixture melting point determination and ultraviolet and infrared spectral comparisons.

Impure XIX evolves hydrogen fluoride slowly at room temperature. In some solvents, for example, benzene and chloroform, pure XIX decomposes at room temperature slowly, and considerably more rapidly on heating.

**Reduction of 1,4-Difluoro-1,1,4,4-tetraphenylbutane (XIX).**

**A. With Lithium Aluminum Hydride.**—To a suspension of 200 mg. of lithium aluminum hydride in 12 ml. of tetrahydrofuran was added 100 mg. of 1,4-difluoro-1,1,4,4-tetraphenylbutane. The reaction mixture was stirred and heated under reflux in a nitrogen atmosphere for 47 hours, cooled to room temperature, and treated successively with 4 ml. of ethyl acetate, 2 ml. of 95% ethanol and 10 ml. of 6 *N* hydrochloric acid. The mixture was extracted with two 30-ml. portions of ether and the combined extracts were washed successively with water (twice), sodium bicarbonate solution and water (twice). The dried solution (over sodium sulfate) was concentrated and the crystalline residue was chromatographed on neutral alumina (hexane–benzene). The fraction with m.p. 113–116° was recrystallized twice from hexane to give 28 mg. (31%) of 1,1,4,4-tetraphenylbutane, m.p. 121–122° (lit.<sup>13</sup> 120–121°) which was shown by a mixture melting point determination and infrared spectral comparison to be identical with an authentic specimen.<sup>13</sup>

**B. With Lithium Aluminum Deuteride.**—1,4-Dideuterio-1,1,4,4-tetraphenylbutane, m.p. 121.6–122.0°, was prepared in 33% yield by the reduction of 660 mg. of 1,4-difluoro-1,1,4,4-tetraphenylbutane with 400 mg. of lithium aluminum deuteride in 20 ml. of tetrahydrofuran according to the procedure described above. Its infrared spectrum in carbon tetrachloride solution exhibited medium intense absorption at 4.71  $\mu$  (C–D stretching) and its n.m.r. spectrum, unlike that of unlabeled

(32) A. Klages, *Ber.*, **35**, 2646 (1902).

(33) The preparation of iodobenzene difluoride and the fluorination of the propene were carried out in polyethylene ware.

(34) H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954).

(35) J. Salkind and V. Teterin, *Ber.*, **62**, 1748 (1929).

1,1,4,4-tetraphenylbutane, showed no peak at 6.17  $\tau$  for benzydrylic hydrogen. Mass spectrometry showed the compound to have mol. wt. 364 and to contain two deuterium atoms per molecule.<sup>30</sup>

**Methanolysis of 1,4-Difluoro-1,1,4,4-tetraphenylbutane (XIX).**—A mixture of 100 mg. (0.25 mmole) of 1,4-difluoro-1,1,4,4-tetraphenylbutane, 5.0 ml. of dioxane and 14 ml. of methanol was heated to boiling. After 5 minutes of boiling, an additional 1.0 ml. of dioxane was added to the suspension and as soon as the last traces of solid had dissolved a solution of 2 drops of concentrated sulfuric acid in 2.0 ml. of methanol was added. The solution was maintained at the reflux temperature for 20 minutes, treated again with concentrated sulfuric acid (1 drop) in methanol (1.0 ml.), and allowed to cool to room temperature. From the light green solution, 63 mg. of colorless needles, m.p. 199–217°, separated after standing overnight at room temperature. Three recrystallizations of this material from toluene gave 30 mg. (27%) of 1,4-dimethoxy-1,1,4,4-tetraphenylbutane, m.p. 233–234° (lit.<sup>14</sup> 230°), which was shown by a mixture melting point determination and infrared and ultraviolet spectral comparisons to be identical with an authentic sample.<sup>14</sup>

**2-Chloro-1-fluoro-1,1-diphenylethane (XXI).**—Following the procedure described above for the preparation of 1,2-difluoro-1,1-

diphenylethane (I), 1.00 g. (4.3 mmole) of 2-chloro-1,1-diphenylethane<sup>6</sup> was converted by the action of 0.5 ml. of anhydrous hydrogen fluoride at Dry Ice temperature for 1 minute to 2-chloro-1-fluoro-1,1-diphenylethane. One recrystallization from methanol afforded 0.71 g. (70%) of analytically pure XXI as white crystals, m.p. 52.7–53.2°.

*Anal.* Calcd. for  $C_{14}H_{12}ClF$ : C, 71.64; H, 5.16. Found: C, 71.70; H, 5.20.

Heating of XXI at 110° caused an immediate evolution of hydrogen fluoride; 2-chloro-1,1-diphenylethylene, m.p. 41.5–42.5° (from methanol) (lit.<sup>19</sup> m.p. 42°), identified by a mixture melting point determination and infrared spectral comparison with an authentic sample,<sup>19</sup> was formed.

Purified XXI appears to have the same stability characteristics as 1,2-difluoro-1,1-diphenylethane (I).

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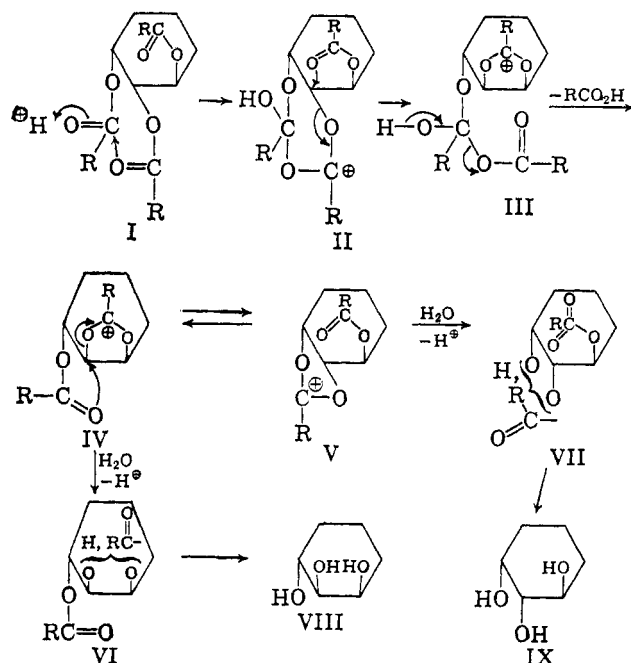
## Behavior of Esters in Liquid Hydrogen Fluoride. Walden Inversion in Tetrahydropyran Derivatives

BY E. J. HEDGLEY<sup>1</sup> AND HEWITT G. FLETCHER, JR.

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The effect of liquid hydrogen fluoride upon the esters of four polyhydroxytetrahydropyrans (1,5-anhydroglycitols) is predicted on the basis of earlier experience with esters of hexahydroxycyclohexanes. In each case, experiment confirmed prediction, Walden inversion taking place only at the central carbon atom of a contiguous *cis-trans*-triacyloxy sequence.

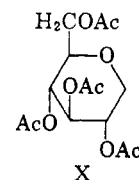
It has recently been shown<sup>2</sup> that esters of a variety of



polyhydroxycyclohexanes undergo deacylation with Walden inversion when treated with liquid hydrogen fluoride. From the examples studied, the stereochemical feature common to these reactions appears to be the inversion of the configuration of the middle carbon atom of a contiguous *cis-trans* sequence of acyloxy groups. A mechanism, illustrated by the simplified

formulas I to IX, was proposed to explain the observed facts. With acetyl groups, complete deacetylation results, the end products being the triol IX, having the configuration of the original ester used (I), and the diastereoisomeric triol VIII.<sup>3,4</sup> In order to explore further the utility of this reaction and to confirm or refute the generalizations offered earlier, we have now turned our attention to the esters of certain hydroxylated tetrahydropyrans, *viz.*, the 1,5-anhydroalditols.

2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol (X)



may be considered first. Here, in the absence of a *cis* pair of acyloxy groups, initial ring formation as in II is excluded and thus, barring the intervention of other mechanisms, X should simply be deacetylated by the

(3) Obviously, substituents other than those shown in formulas I to IX would be required in order to make VIII and IX diastereoisomers.

(4) S. J. Angyal, P. A. J. Gorin and M. Pitman [*Proc. Chem. Soc.*, 337 (1962)] have shown recently that the acetates of some cyclitols as well as the cyclitols themselves undergo partial Walden inversion when refluxed with 95% acetic acid containing 1.5% sulfuric acid. Here the stereochemical requirements for the inversion appear to be the same as those which were found for rearrangements in hydrogen fluoride.<sup>2</sup> However, there is a fundamental difference between the two processes: With anhydrous hydrogen fluoride the mechanism involves an essentially irreversible deacetylation, whereas the rearrangements in the aqueous acetic acid-sulfuric acid system are carried out under conditions which permit re-esterification of deacetylated species and the establishment of a true equilibrium. It is not surprising, therefore, that the proportion and nature of the products in the two processes differ. Thus, Angyal, Gorin and Pitman found *epi*-inositol to give a mixture of *epi*-, *allo*- and *neo*-inositols in the proportion of 17:23:60, while we found<sup>2</sup> that *epi*-inositol hexaacetate in hydrogen fluoride gives a mixture of *epi*- and *allo*-inositols only, no trace of the readily recognizable *neo*-inositol being detected.

(1) Visiting Associate, 1961–1963; permanent address: Department of Chemistry, Birkbeck College, London, W.C. 1.

(2) E. J. Hedgley and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **84**, 3726 (1962).