an identical retention time with a saturated estrane standard, *i.e.*, $3\alpha,17\beta$-dihydroxy-$5\beta(10\beta)$-estrane (III), and the minor compound a glpc retention time similar to a $3\alpha,17\beta$-dihydroxy-5(10)-estrene (II) standard.

B. Na_2SO_3 0.5 × 10^{-1} *M* and Estradiol 5.4 × 10^{-3} *M*. This experiment represents a one-half decrease in sodium sulfite concentration and twofold increase in $3,17\beta$-estradiol concentration in relation to the experiment described above. A solution of 1.306 g of $3,17\beta$-estradiol and 384 mg of sodium hydroxide in 300 ml of ethanol was added to 6.0 g of sodium sulfite in 600 ml of water. The solution was irradiated and the ultraviolet absorption band at 297 $m\mu$ recorded using optical density units at the following times (in hours): 0, 2.09; 2, 1.85; 6, 1.41; 19, 0.58; 27, 0.28; 44, 0.04. The reaction mixture was worked up in the usual manner, the chloroform extract amounting to 664 mg of pale yellow solid (*ca.* 50%). The glpc chromatogram of the material showed the presence of two reduced compounds (3.4 and 4.5 min) in the same ratio as found in the foregoing experiment.

C. Absence of Additional Base. A solution of 653 mg (2.4 mmoles) of $3,17\beta$-estradiol in 300 ml of ethanol was added to 24.0 g (0.19 mole) of sodium sulfite in 600 ml of water. The resulting clear solution was photoreduced for 24 hr. This disappearance of the aromatic absorption band at 288 $m\mu$ was recorded using optical density units at the following times (in hours): 0, 1.63; 1, 1.60; 2, 1.42; 4, 1.17; 7, 0.83; 12, 0.50; 18, 0.27; 24, 0.13. The chloroform-soluble extract gave 380 mg of colorless solid (*ca.* 58%). The glpc chromatogram showed peaks at 3.4 and 4.5 min as previously described. Ten similar irradiations were carried out. The combined chloroform extracts from each amounted to 3.76 g of crude photoreduced material which was chromatographed on 165 g of alumina (Woelm, neutral grade 1). Elution with 1.7 l. of 0.25% methanol in ether gave 474 mg of colorless solid enriched in the two photoreduced monomers. This material was chromatographed on 25 g of alumina. Elution with 0.17 and 0.25% methanol in ether gave 104 and 118 mg of photoproduct, respectively, whose glpc chromatograms showed a single peak at 3.4 min corresponding to the major photoreduced compound (*ca.* 70% of the total photoreduced monomers). The combined material (222 mg) was crystallized from acetone to give 177 mg of colorless flakes, mp 160–165°, sintering at 130°. Two recrystallizations from acetone–methanol gave $3\beta,17\beta$-dihydroxy-$5\alpha,10\beta$-estrane (IV), mp 175–177°, $[\alpha]^{22}D$ +32.2° ($CHCl_3$). Two additional recrystallizations from ethyl acetate did not raise the melting point [lit.[11] mp 171–173°, $[\alpha]^{26}D$ +26° ($CHCl_3$)].

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.44; H, 10.90.

Dihydroxy-$5\alpha,10\beta$-estrane (15.3 mg) was acetylated with 0.2 ml of acetic anhydride and 1.0 ml of pyridine. The solution was heated for 2 hr at 80° and then kept at room temperature overnight. The reaction mixture was slowly added, with stirring, to 10 ml of ice water. The colorless solid was removed by filtration and washed with water. The product was crystallized from ethanol–water to give $3\beta,17\beta$-diacetoxy-$5\alpha,10\beta$-estrane as colorless flakes, mp 145–147° (lit.[11] mp 142–145°).

The minor monomeric photoreduction product (4.5-min glpc retention time) was found to be present in the 0.5 and 1% methanol–ether elutions of the initial chromatographic separation. The compound (*ca.* 30% of total monomer yield) was not isolated in pure form.

Elution of the chromatographic column with more polar solvent (5, 25, and 50% methanol in ether) gave polymeric material (*ca.* 56% of the chloroform-soluble extract) which was not detected by glpc.

Photoreduction of $3,17\beta$-Estradiol. A. With Sodium Bisulfite. A solution of 544 mg (2 mmoles) of $3,17\beta$-estradiol and 160 mg of sodium hydroxide in 250 ml of ethanol was added to a solution of 8.3 g (0.08 mole) of sodium bisulfite ($NaHSO_3$) in 500 ml of water. A small amount of bisulfite precipitated which was removed by filtration. The solution was irradiated for 18 hr. An aliquot of the solution showed no aromatic ultraviolet absorption at 297 $m\mu$. The chloroform extract gave 70 mg (*ca.* 13%) of colorless solid. A glpc chromatogram of the product showed a single peak at 3.4 min, identical with the retention time of $3\beta,17\beta$-dihydroxy-$5\alpha,10\beta$-estrane (IV).

An increase in yield of the chloroform-soluble extract (31%) was obtained by irradiation (20 hr) in which the sodium bisulfite concentration was increased twofold and in the absence of sodium hydroxide. The material consisted of two photoreduced monomers with identical glpc retention times as the compounds from the sodium sulfite reaction.

B. With Sodium Metabisulfite. A solution of 544 mg of $3,17\beta$-estradiol and 160 mg of sodium hydroxide in 250 ml of ethanol was added to 15.2 g (0.08 mole) of sodium metabisulfite ($Na_2S_2O_5$) in 500 ml of water. The cloudy solution was irradiated for 18 hr. The ultraviolet absorption at 297 $m\mu$ of an aliquot of the solution had decreased to zero. The chloroform extract gave 92 mg (17%) of colorless solid, a glpc chromatogram of which indicated the presence of a single photoreduced monomer identical with estrane IV.

C. With Sodium Hydrosulfite. $3,17\beta$-Estradiol was irradiated for 18 hr as described above in the presence of sodium hydrosulfite ($Na_2S_2O_4$). A glpc chromatogram of the chloroform-soluble extract (65 mg, 12%) displayed a single peak whose retention time corresponded to compound IV from the sodium sulfite reaction.

Attempted Photoreductions. A. Sodium Thiosulfate. $3,17\beta$-Estradiol (544 mg) was photolyzed (18 hr) in the manner described above in the presence of 19.8 g (0.08 mole) of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$). The solution turned deep red in color after a few minutes of irradiation. The chloroform extract gave a dark brown solid (132 mg) consisting of starting material and no detectable amount of photoreduced monomer by glpc.

B. Sodium Dithionate. Irradiation of $3,17\beta$-estradiol (544 mg) for 24 hr in the presence of sodium dithionate (19.4 g, 0.08 mole, $Na_2S_2O_6 \cdot 2H_2O$) gave 348 mg of dark brown solid. The glpc chromatogram of the material indicated the absence of any reduced monomer.

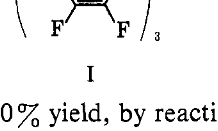
Acknowledgment. The initial observations on the photoreduction of phenols were made by Dr. P. Cerutti, now Department of Chemistry, Princeton University, and Dr. James A. Moore, then Visiting Professor from the University of Delaware. Preliminary experiments on the photoreduction of estradiol were carried out by Dr. M. Chaykovsky. We are greatly indebted to Professor Robert M. Moriarty, Catholic University of America, for constructive criticism of the manuscript.

Communications to the Editor

Tris(pentafluorophenyl)methyl Cation

Sir:

We wish to report the preparation and spectroscopic detection of tris(pentafluorophenyl)methyl cation (I).



I

Tris(pentafluorophenyl)carbinol (II), mp 116–117° (cor), was prepared in 72% yield by reaction of decafluorobenzophenone[1] with pentafluorophenyllithium (from C_6F_5Br + *n*-BuLi) in *n*-hexane solution at −78° or preferably, in 60% yield, by reaction of pentafluorophenyllithium with ethyl pentafluorobenzoate in ether at −65° (*Anal.* Calcd for $C_{19}HOF_{15}$: C, 43.04; H,

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

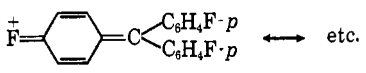
0.19. Found: C, 42.77; H, 0.24), ν_{OH} 3600 cm^{-1}, pmr (CCl_4): τ 5.82 (septuplet), J_{HF} = 3.0 cps [triphenylcarbinol: τ 7.23 (multiplet), J_{HH} = 1.0 cps].

When II was dissolved in 100% H_2SO_4 at room temperature, a pink solution formed immediately. The visible spectrum of this solution exhibited strong absorption, $\lambda_{max}^{H_2SO_4}$ 500 mμ (log ϵ 4.63). We attribute this behavior to the presence of cation I. Triphenylmethyl cation possesses bands at 428 and 409 mμ (log ϵ 4.58).[2] Compound II is regenerated when the acid solution is poured into water. Support for the existence of the cation was found by hydride exchange with cycloheptatriene.[3] The mixture was added to water and, after extraction with carbon tetrachloride and evaporation of solvent, a white solid, tris(pentafluorophenyl)methane, $(C_6F_5)_3CH$ (III), mp 158.0–159.5° (cor) (CH_3OH), was isolated (*Anal.* Calcd for $C_{19}HF_{15}$: C, 44.38; H, 0.19. Found: C, 44.19; H, 0.44); pmr (CCl_4): τ 3.80 (multiplet), substantially deshielded with reference to $(C_6H_5)_3CH$ (τ 4.54). Compound III was also prepared in 70% yield by reaction of II with phosphorus tribromide. No halide could be isolated. The mechanism of this reaction is under study.

Cation I is very unstable in sulfuric acid solution relative to triphenylmethyl cation. In 96% H_2SO_4, the half-life of I is about 2 min at room temperature. The development of a second band at shorter wavelength is observed within a few minutes. The nature of the species being formed is under investigation.

The transiency of I makes it difficult to obtain a quantitative measure of its stability, but it appears that the alcohol is half-ionized in 93% H_2SO_4, so that the pK_{R^+} of II is about -17.5, while that of triphenylcarbinol is -6.63.[4] The instability of I reflects the increased localization of the positive charge on the methinyl carbon, due to repulsion of the charge by the C–F bond dipoles.

We have also prepared 4,4′,4′′-trifluorotriphenylcarbinol (IV), mp 91–92.5°, by reaction of ethyl *p*-fluorobenzoate with excess *p*-fluorophenylmagnesium bromide (*Anal.* Calcd for $C_{19}H_{13}OF_3$: C, 72.61; H, 4.17. Found: C, 72.86; H, 4.28). Compound IV forms a carbonium ion in sulfuric acid solution (λ_{max} 433 mμ) which is more stable (pK_{R^+} = -6.05) than triphenylmethyl cation. In this case, resonance stabilization by participation of the *p*-fluorine atoms (V) outweighs the destabilization due to the inductive effect.



V

In contrast, the over-all polar effect of the pentafluorophenyl group is the overwhelming factor, and resonance is of little significance.

Further studies on these and related compounds will be reported in a full paper.[5]

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(2) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 458.

(3) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harman, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(4) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

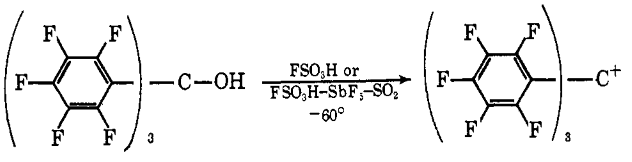
(5) Note Added in Proof. The method of choice for the preparation of II is the reaction of diethyl carbonate with 3 equiv of C_6F_5Li at $-25°$. The yield is better than 50%.

Stable Carbonium Ions. XXXV.[1] Pentafluorophenylcarbonium Ions

Sir:

Tri-, di-, and monophenylcarbonium ions are well investigated (ultraviolet, infrared, nmr, X-ray studies).[2] In extension of our previous work on fluoroalkylcarbonium ions[3] we felt it was of interest to extend our investigations to fluorophenylcarbonium ions. The fluorine nmr shifts are much larger than the pmr shifts, and therefore anisotropy and other effects influence the effect of a positive charge on chemical shifts to a lesser degree. We wish now to report the observation of the tris-, bis-, and monopentafluorophenylcarbonium ions and their nmr study.

Tris(pentafluorophenyl)carbinol[4a] gives a relatively unstable solution in sulfuric acid.[4b] It was, however, found that its solution in fluorosulfonic acid or fluorosulfonic acid–antimony pentafluoride at $-60°$ is stable and allows the observation of the ^{19}F magnetic resonance spectrum (Figure 1) of tris(pentafluorophenyl)carbonium ion (I). In $FSO_3H–SbF_5$ solution the ^{19}F nmr shift of the *p*-fluorine atoms is underlying the broad Sb–F resonance. This interference can be eliminated by using neat fluorosulfonic acid as solvent. The ^{19}F resonance spectrum of ion I when compared with that of starting tris(pentafluorophenyl)carbinol (II; Table I) shows substantial deshielding of the *ortho*, *meta*, and *para* ring fluorine atoms ($\Delta\delta_{ortho}$ = 14.7 ppm, $\Delta\delta_{meta}$ = 6.21 ppm, and $\Delta\delta_{para}$ = 40.1 ppm). The largest deshielding effect (40.1 ppm) is observed in the case of the *p*-fluorine atoms. This clearly indicates the high degree of charge delocalization into *ortho* and *para* positions in ion I and the importance of resonance forms of quinoidal nature.



I

Taft's observation[5] of fluorine nmr shielding in monofluorophenyl cations in strong acid media is also in accordance with this observation.

The bis(pentafluorophenyl)carbonium ion II can

(1) Part XXIV: G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Am. Chem. Soc.*, in press.

(2) For a summary see G. A. Olah and M. W. Meyer in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Wiley-Interscience Publishers, Inc., New York, N. Y., 1963, Chapter VIII.

(3) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **88**, 3310 (1966).

(4) (a) We are grateful to Professor R. Filler for a sample of tris(pentafluorophenyl)carbinol; (b) see R. Filler, C.-S. Wang, M. A. McKinney, and F. N. Miller, *J. Am. Chem. Soc.*, **89**, 1026 (1967), indicating half-protonation in 93% H_2SO_4.

(5) Professor R. W. Taft, Jr., personal communication.