

Photochemical Reactions of Benzene with Trifluoroacetic Acid and $\alpha\alpha\alpha$ -Trifluoroacetophenone

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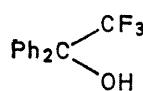
Summary $\alpha\alpha\alpha$ -Trifluoroacetophenone is the primary product of the light-induced reaction between benzene and trifluoroacetic acid and a novel acid-catalysed photoaddition of this ketone to benzene subsequently occurs; irradiation of acetyl chloride in benzene gives acetophenone.

that another was probably the (\pm)-isomer of the diol (II). Traces of biphenyl were detected.

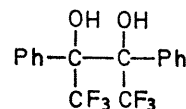
THE use of trifluoroacetic acid as a proton source for the detection of polarised intermediates in photochemical reactions has been described.¹ We now report that photoreaction between trifluoroacetic acid and benzene gives $\alpha\alpha\alpha$ -trifluoroacetophenone (*cf.* the reported 1,3-addition of acetic acid²). Several secondary photoproducts are also produced, including 2,2,2-trifluoro-1,1-diphenylethanol (I) which results from a novel type of acid-catalysed photoaddition of the first formed trifluoroacetophenone to benzene.

Irradiation of a mixture of benzene and trifluoroacetic acid (4:1 molar ratio; low- or medium-pressure Hg lamp; 24 hr†), followed by distillation of the products up to 190° and 0.2 mmHg to separate them from ill-defined 'polymeric' material, gave a mixture, the major component of which was *meso*-1,1,1,4,4,4-hexafluoro-2,3-diphenylbutan-2,3-diol (II)‡, identical with the product from the known photoreduction of trifluoroacetophenone in propan-2-ol.³

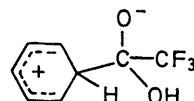
The other main component was $\alpha\alpha\alpha$ -trifluoroacetophenone. Of the numerous minor products, the most abundant was 2,2,2-trifluoro-1,1-diphenylethanol (I),§ and combined gas chromatography-mass spectrometry indicated



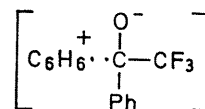
(I)



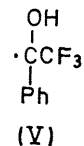
(II)



(III)



(IV)



(V)

Irradiation of a mixture of benzene, trifluoroacetic acid, and trifluoroacetophenone (35:2:3 molar ratio) through a Pyrex filter using a medium-pressure Hg lamp resulted in the ready formation of the same products in approximately the same ratios as found in irradiation of benzene and trifluoroacetic acid alone. Methanol could be used as

† All photochemical reactions reported here were carried out at 15° under nitrogen and in fused silica apparatus unless otherwise specified. No reactions occurred in the absence of u.v. radiation, except in the case of t-butyl chloride.

‡ The configuration was determined by an X-ray crystallographic analysis of the dimethyl ether of (II). We thank Dr. M. G. B. Drew for his collaboration in this work.

§ Identified by a comparison of its mass spectrum and g.l.c. retention times (3 columns) with those of an authentic sample.⁴

proton source in place of trifluoroacetic acid, although some additional products, as yet unidentified, were also formed. Benzene and trifluoroacetic acid did not react when irradiated through a Pyrex filter ($\lambda > 290$ nm). Benzene and trifluoroacetophenone did not react when irradiated in the absence of trifluoroacetic acid, nor did trifluoroacetophenone and trifluoroacetic acid photoreact in the absence of benzene. These findings contrast interestingly with Wagner and Leavitt's recent report that the photopinacol reduction of trifluoroacetophenone by alkylbenzenes such as toluene occurs in the absence of added acid where the alkyl group acts as a hydrogen (probably proton) donor.⁵ These workers suggested the possibility of charge-transfer quenching of triplet trifluoroacetophenone by benzene, but did not note any charge-transfer absorption.

On the other hand, we find that thin-film u.v. spectra⁶ of mixtures of benzene and trifluoroacetophenone show an additional absorption at 268 nm, in the presence and absence of trifluoroacetic acid. This seems reasonably attributable to a charge-transfer transition between benzene and the ketone since no additional absorption is shown by comparable mixtures of benzene and the weaker acceptor acetophenone. Thus the previous proposal⁵ that charge-transfer to trifluoroacetophenone from the benzene ring follows preliminary excitation of the ketone needs reconsideration.

Mixtures of benzene and trifluoroacetic acid show an additional absorption at 217 nm, possibly attributable to excitation of the benzenonium ion,⁷ but it appears difficult to involve this ion in a mechanism which accounts adequately for the formation of trifluoroacetophenone. The results are more consistent with charge-transfer from unprotonated S_1 benzene to trifluoroacetic acid to give a spin-coupled radical-ion pair or polarised exciplex which transforms into the zwitterionic intermediate (III) (or an

analogous polarised diradical if T_1 benzene is the donor) *en route* to $\alpha\alpha\alpha$ -trifluoroacetophenone. Likewise, photochemical charge-transfer from benzene to trifluoroacetophenone through the absorption band centred at 268 nm should give rise initially to the spin-paired radical-ion pair (IV) which becomes stabilised by radical combination and protonation on oxygen (not necessarily in that order) and then undergoes deprotonation from carbon to give the alcohol (I). Competitive diffusion of the radical (V) from the solvent cage would satisfactorily account for the pinacol (II). Evidently little proton-transfer from $C_6H_6^+$ occurs, since only traces of biphenyl were formed (*cf.* ref. 5). Neither acetophenone nor *p*-cyanoacetophenone underwent a photoreaction with benzene in the presence or absence of trifluoroacetic acid.

The formation of trifluoroacetophenone from benzene and trifluoroacetic acid is an example of photo-Friedel-Crafts acylation (*cf.* ref. 1). Some related systems have also been investigated. Thus, irradiation of acetyl chloride in benzene gave acetophenone. Added hydrogen chloride had no effect on the reaction, and irradiation of acetyl chloride and benzene in the presence of tetraphenyltin (as an acid scavenger) also produced acetophenone, although other products, apparently originating from the tetraphenyltin, were also formed. In contrast, acetic anhydride was photochemically unreactive towards benzene.

Irradiation of *t*-butyl chloride in benzene gave no *t*-butylbenzene. Irradiation in the presence of hydrogen chloride gave a little *t*-butylbenzene (by a *thermal* reaction), together with small amounts of four products having $M = 150$ (mass spectrometer) corresponding to 2:1 adducts of hydrogen chloride and benzene. These were not found after irradiation of benzene-HCl alone, and are under further investigation.

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¹ D. Bryce-Smith, R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561.

² E. Farenhorst and A. F. Bickel, *Tetrahedron Letters*, 1966, 5911; *cf.* L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1966, **88**, 2881.

³ W. A. Mosher and N. D. Heindel, *J. Amer. Chem. Soc.*, 1963, **85**, 1548.

⁴ G. A. Olah and C. V. Pittman, *J. Amer. Chem. Soc.*, 1966, **88**, 3310.

⁵ P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, 1970, **92**, 5806.

⁶ D. Bryce-Smith, B. E. Connett, and A. Gilbert, *J. Chem. Soc. (B)*, 1968, 816. The spectra were plotted using a computer-based technique which will be described elsewhere.

⁷ D. Bryce-Smith and G. B. Cox, following communication.