The 2,2,2-Triphenylethyl Radical[1]

Sir:

We wish to report the generation and efficient trapping of the free 2,2,2-triphenylethyl radical. This radical, which apparently possesses an extremely great tendency to rearrange, has not previously been observed as a kinetically free species, all attempts[2] at its generation having led to products derived from the 1,1,2-triphenylethyl radical.

Our method involved the reduction of 2,2,2-triphenylethyl chloride to 1,1,1-triphenylethane by triphenyltin hydride, a reaction whose course is proposed to be

$$Ph_3Sn\cdot + Ph_3CCH_2Cl \longrightarrow Ph_3SnCl + Ph_3CCH_2\cdot$$

$$Ph_3CCH_2\cdot + Ph_3SnH \longrightarrow Ph_3CCH_3 + Ph_3Sn\cdot, \text{ etc.}$$

by analogy with the reduction by triphenyltin hydride of other halides.[4]

Table I summarizes the results obtained at several temperatures and two concentration ranges.

Table I. Summary of Results

Reagents, mmoles		Solvent (benzene), ml	Temp, °C	% Ph_3CCH_3[b]
Ph_3CCH_2Cl[a]	Ph_3SnH			
0.27	1.43	0.10	68	>90
0.27	1.44	0.10	84	83
0.29	1.43	0.10	101	76
0.34	1.46	0.10	132	62
0.28	0.29	0.25	85	40
0.29	0.42	0.25	100	40
0.25	0.38	0.25	132	27

[a] The chloride, rather than the bromide or iodide, has been used because of its greater accessibility [H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5456 (1957)]. Since higher temperatures favor rearrangement and since the bromide and iodide require much lower temperatures for reaction than the chloride does, use of the iodide in particular would probably eliminate the necessity of using a large excess of triphenyltin hydride in order to achieve complete trapping. [b] Based on complete consumption of the 2,2,2-triphenylethyl chloride. The other major product was 1,1,2-triphenylethane.

The usefulness of the reaction between organic halides and triorganotin hydrides as a means of conveniently and cleanly[5] generating free radicals has become clear recently. The present work indicates the potential of the reaction as a means of intercepting radicals which are highly prone to rearrange configurationally or structurally and, hence, of studying the rearrangement process.

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[2] A variety of methods has been tried, including the use of aldehyde decarbonylation,[3a,b] decomposition of azo compounds,[3c] the Hunsdiecker reaction,[3d] peroxide decomposition,[3e,f] and Kolbe electrolysis.[3g]

[3] (a) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952); (b) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); (c) D. Y. Curtin and T. C. Miller, *ibid.*, **25**, 885 (1960); (d) J. W. Wilt and D. D. Oathoudt, *ibid.*, **23**, 218 (1958); (e) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Am. Chem. Soc.*, **86**, 1116 (1964); (f) W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 3960 (1963); (g) H. Breedeweld and E. C. Kooyman, *Rec. Trav. Chim.*, **76**, 297 (1957). Denney,[3e] in a study of the decomposition of 2,2,2-triphenylpropanoyl peroxide, reported the formation, in a "cage combination," of 4% of 1,1,1,4,4,4-hexaphenylbutane. Professor Denney, in a private communication, has informed us that he is currently studying the reaction of triphenylmethyl with diazomethane [W. Schlenk and C. Bornhardt, *Ann.*, **394**, 183 (1912); E. Mueller, A. Moosmayer, and A. Rieker, *Z. Naturforsch.*, **18b**, 982 (1963)], a reaction which he believes involves the 2,2,2-triphenylethyl radical.

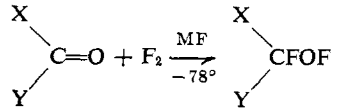
[4] D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963); E. P. Kupchik and R. J. Kiesel, *ibid.*, **29**, 764, 3690 (1964); L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

[5] We feel that there are two principal advantages of this method. The desired radical is formed directly from the starting material without the intermediacy of other radicals which can also enter into reactions, as in, for example, reactions involving acyloxy or acyl radicals. Also, a wide range of temperature, determined by which halide is the precursor, is available for generating the desired radical.

A Simple Synthesis of Fluoroxyperfluoroalkyl Compounds

Sir:

Until recently the only known example of an organic fluoroxy compound was CF_3OF.[1] It was formed by fluorination of carbon monoxide, carbonyl fluoride, or methanol over a silver fluoride catalyst at 160–180°. Several other monofluoroxy derivatives have recently been reported (*e.g.*, C_2F_5OF, C_3F_7OF, $(CF_3)_3COF$, and $(CF_3)_2CFOF$).[2] They were prepared by the reaction of fluorine with the corresponding partially fluorinated alcohols under mild conditions. The yields of these new compounds were in general quite low (except when perfluoro-*t*-butyl alcohol was employed), and numerous side products were formed. The bis(fluoroxy)perfluoropropane, $FOCF_2CF_2CF_2OF$, has also been obtained in very low yield (2%) by the fluorination of 1-hydroxy-3-trichloroacetoxypropane.[3] We wish to report a general synthesis for perfluoro organic fluoroxy derivatives in which side reactions are generally avoided. The basic reaction is the catalyzed addition of fluorine across the carbon–oxygen double bond in a perfluorocarbonyl compound.



$$XYC{=}O + F_2 \xrightarrow[-78°]{MF} XYCFOF$$

$X = R_f$ or F, $Y = R_f$ or F, M = K, Rb, or Cs

The addition occurs in an almost quantitative manner when carried out in a static system.[4] If the stoichiometric amount of fluorine is used, cleavage of the carbon skeleton is all but eliminated. The following conversions were accomplished: $COF_2 \rightarrow CF_3OF$, 97% yield; $CF_3C(O)F \rightarrow C_2F_5OF$, 96% yield; $C_2F_5C(O)F \rightarrow C_3F_7OF$, 97% yield; and $(CF_3)_2C{=}O \rightarrow (CF_3)_2CFOF$, 98% yield. The products were identified by comparison of their infrared and ^{19}F nmr spectra with those in the literature[1,2,5] and by vapor density molecular weight determinations. The purity (or yield) of the crude products was determined by vapor phase chromatography using the column recommended in the literature.[2]

The reaction was quite rapid at −78° in the presence of alkali metal fluorides. No apparent differences in

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[1] G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953).

[2] J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

[3] J. H. Prager, *J. Org. Chem.*, **31**, 392 (1966).

[4] Monel or stainless steel Hoke cylinders were generally employed in this study although dried glass bulbs could also be used.

[5] G. H. Cady and C. I. Merrill, *J. Am. Chem. Soc.*, **84**, 2662 (1962).