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	Temp,	%
$Ph_3CCH_2Cl^a$	Ph_3SnH	(benzene), ml	°C	$Ph_3CCH_3{}^b$
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.

Acknowledgments. We are grateful to M & T Chemicals for a gift of triphenyltin chloride and to the National Science Foundation for funds for the purchase of a Varian A-60 nmr spectrometer.

Leonard Kaplan
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received July 27, 1966

---

[1] This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

[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.

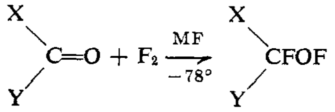
[4] D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963); E. P. Kupchik and R. J. Kiesel, *ibid.*, **29**, 764, 3690 (1964); L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

[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.



$$X(Y)C{=}O + F_2 \xrightarrow[-78^\circ]{MF} X(Y)CFOF$$

$X = R_f$ 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

---

[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).

the course or rate of reaction were noted when either potassium fluoride, rubidium fluoride, or cesium fluoride was employed as a catalyst. However, when the reaction between either $CF_3C(O)F$ or $(CF_3)_2C{=}O$ and fluorine was carried out in the complete absence of metal fluorides, no formation of the fluoroxy derivatives was observed. In fact, no reaction was noted at −78°. Although the role of the metal fluoride is not known with certainty, it is likely that an ionic intermediate such as $XYCFO^-$ is the active species involved in the fluorination. Support for this assumption was obtained by fluorination of the salt, $CsOCF_3$,[6] under similar conditions. Fluoroxytrifluoromethane was produced in quantitative yield.

Several attempts were made to extend the catalytic fluorination procedure to other carbonyl derivatives. When phosgene was allowed to react with fluorine in equimolar quantities at −78°, the following reaction was observed. Half of the phosgene initially charged

$$COCl_2 + 2F_2 \longrightarrow CF_3OF + Cl_2$$

was recovered unchanged. Fluorination of $HCF_2C(O)F$ over cesium fluoride at 0° produced an unstable material which was contaminated with small amounts of COF_2, HCF_3, and CF_4. Attempted purification of this product by vacuum line fractionation resulted in spontaneous and often violent decomposition. The ^{19}F nmr spectrum of the crude product in CF_3Cl consisted of an unresolved broad singlet at ϕ −131, an unresolved singlet at ϕ 99.9, and a doublet at ϕ 136.4, $J_{HF} = 56$ cps. The relative area ratios of the peaks are 1:2.1:1.9. This spectrum is consistent with the formulation of the product as HCF_2CF_2OF if it is assumed that coupling between the CF and OF fluorines is not observed.[7] The infrared spectrum shows no carbonyl absorptions other than trace amounts of carbonyl fluoride and has a weak band in the fluoroxy region[2] which is not present in the starting material. Due to the instability of the product no elemental analyses were obtained.[8]

Acknowledgement. This work was carried out under Army Ordnance Contract Da-01-021 ORD-11878(Z) Modification No. 11.

---

(6) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, 43, 1893 (1965).

(7) The ^{19}F nmr spectrum of C_2F_5OF consists of three groups of bands at ϕ − 139.4 (OF), +97.9 (CF_2), and 82.1 (CF_3).

(8) Caution should be exercised in working with fluoroxy compounds since they are potentially dangerous.

John K. Ruff, Anthony R. Pitochelli, Max Lustig
Rohm and Haas Company, Redstone Research Laboratories
Huntsville, Alabama 35807

Received July 18, 1966

A Nuclear Magnetic Resonance Method for Relative Carbonium Ion Stabilization Energies

Sir:

Quantitative determination of carbonium ion stabilities is a cornerstone in the construction of a compatible structure–reactivity relationship for reactions involving cationic intermediates. In principle, a direct measure of relative carbonium ion stabilities is derived from the equilibrium amounts of a stable carbonium ion in equilibrium with its un-ionized precursor. In practice, useful data have been obtained from carbinol–carbonium ion ionization equilibrium data in strongly acidic media[1] and from the reversible electrode potential reduction method, recently developed by Taft.[2] To these pK_{R^+} and emf methods we now add a convenient nmr technique which promises to be of broad application.

When equimolar amounts of a stable carbonium ion salt (R^+Y^-) and an appropriate carbonium ion precursor (R_0X) are combined in a suitable solvent, rapid exchange of Y^- and X occurs (as shown in eq 1) to yield an equilibrated mixture in which the relative amounts of R^+ and R_0^+ are a direct measure of their free-energy difference (ΔF_0). For convenient analysis of

$$R^+Y^- + R_0X \rightleftharpoons RX + R_0^+Y^- \qquad (1)$$

the equilibrium mixture by nmr it is necessary that the maximum difference in concentration of R^+ and R_0^+ be ~19:1 ($\Delta F° \cong 3.5$ kcal) and that at least one of the components have a single, sharp resonance line, the chemical shift of which is sufficiently different in the covalent and cationic components.[3] The latter requirement is best fulfilled by a methyl or methoxyl substituent, though others (fluoro, dimethylamino, etc.) should prove equally advantageous.

The stability data obtained from (1) are substantially independent of the nonnucleophillic anion (Y^-) and we have found $SbCl_6^-$, BF_4^-, and ClO_4^- to be equally useful. However, the technique for quantitatively estimating the relative amounts of R^+ and R_0^+ depends on the nature of the group X. When the covalent component is a halide (X = Cl or Br) the expected rapid S_N1 exchange occurs between R^+Y^- and RX and between $R_0^+Y^-$ and R_0X, leading to time-averaged resonance lines whose chemical shift is proportional to the mole fraction of each component.[4] For example: mono-*p*-methyltrityl and di-*p*-methyltrityl chlorides in methylene chloride solution display their methyl protons at 139.8 and 138.3 cps[5] while the methyl protons of their respective hexachloroantimonates appear at 164.9 and 163.8 cps. An equimolar mixture of either chloride with the other carbonium ion equilibrates to give lines at 158.0 (six methyl protons) and 145.0 cps (three methyl protons). From these data it is readily calculated that the ratio of di-*p*-methyltrityl to mono-*p*-methyltrityl cations is 78 ± 1:22 ± 1 and that, therefore, $\Delta F° = 1.6 \pm 0.1$ kcal at 40°.

With carbonium ions of $pK_{R^+} > 1$, the halides are partly or completely ionized in solvents which dissolve the carbonium salts and are no longer suitable for exchange (1).[6] However, this by no means limits the utility of the nmr method since we have found that a number of covalent carbonium ion precursors readily participate in the required exchange process (1). Suitable groups (X in RX or R_0X) include methoxy, azide, acetate,

---

(1) (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, 19, 155 (1954); (b) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955); (c) N. C. Deno and A. Schriesheim, *ibid.*, 77, 3051 (1955); (d) N. C. Deno and W. L. Evans, *ibid.*, 79, 5804 (1957).

(2) E. D. Jensen and R. W. Taft, *ibid.*, 86, 116 (1964); R. W. Taft and L. D. McKeever, *ibid.*, 87, 2489 (1965).

(3) Identification of the components of the equilibrium mixture is best accomplished by prior assignment of the resonance lines of the individual species, or, on occasion, by low-temperature techniques.

(4) H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Am. Chem. Soc.*, 86, 4722 (1964).

(5) Downfield from internal TMS; A-60 spectrometer at 40°.

(6) An nmr investigation of the ionization of such halides is currently under investigation.