# Pentafluoroacetone

JOHN B. HYNES, ROSCOE C. PRICE, WALLACE S. BREY, JR.,[1] MICHAEL J. PERONA,[2] AND GLYN O. PRITCHARD[2]

The synthesis of pentafluoroacetone was first described by McBee and his co-workers (1), who prepared it in a low yield by the reaction of ethyl pentafluoroacetoacetate ($CF_3COCF_2COOC_2H_5$) with concentrated acid. They gave a boiling point of 2–3°. The reaction of difluoroacetyl chloride with trifluoromethylmagnesium iodide was also reported to yield pentafluoroacetone, b.p. 4°, in a 59% yield (2).

However, since the successive replacement of chlorine by hydrogen in 1,3-dichlorotetrafluoroacetone causes an increase in the boiling point of the resulting product and since chloropentafluoroacetone boils at 7.8° (3), it was suspected that the literature values for pentafluoroacetone were incorrect. For example, compare the following atmospheric boiling points: $CClF_2COCClF_2$, b.p. 45.2° (3); $CClF_2COCHF_2$, b.p. 50°;[3] and $CHF_2COCHF_2$, b.p. 59° (4,5).

We now report a convenient route to pentafluoroacetone in an 85% yield, a corrected boiling point, and a confirmation of its structure by infrared, nuclear magnetic resonance, and mass spectroscopy and gas-phase photolysis. The method, which was basically that of Middleton and Lindsey (4), involves the reduction of chloropentafluoroacetone with triethyl phosphite. The observed atmospheric boiling point of a large sample having a purity greater than 99.5% (as shown by gas chromatography) was 12.5–13.5°.

The photolysis products were CO, $CF_2H_2$, $CF_3H$, $C_2F_4H_2$, $C_2F_5H$, $C_2F_6$, and $C_3F_8$. A typical mechanism (6) for their formation is as follows.

$$CF_2HCOCF_3 + h\nu \rightarrow CO + CF_2H + CF_3$$
$$2CF_2H \rightarrow C_2F_4H_2$$
$$CF_2H + CF_3 \rightarrow C_2F_5H$$
$$2CF_3 \rightarrow C_2F_6$$

The fluoromethanes may arise from attack on the ketone molecule, e.g.

$$CF_3 + CF_2HCOCF_3 \rightarrow CF_3H + CF_2COCF_3,$$

and from the following disproportionation reactions:

$$CF_2H + CF_2H \rightarrow CF_2H_2 + CF_2$$
$$CF_3 + CF_2H \rightarrow CF_3H + CF_2.$$

The disproportionation/combination ratio for $CF_2H$ radicals is well established as 0.19 (6, 7). The $C_3F_8$ is presumably formed as follows.

$$CF_3 + CF_2 \rightarrow C_2F_5$$
$$C_2F_5 + CF_3 \rightarrow C_3F_8$$

The mass spectrum of the ketone is recorded in Table I, and the large peaks obtained for the alkyl-ion fragments $CF_2H^+$ and $CF_3^+$ are typical of the cracking patterns for perhaloketones (8). The relative abundance of the acetyl-ion fragment ($CF_2HCO^+$) is much greater than that of $CF_3CO^+$. Similar behavior is exhibited by the unsymmetrical fluoroketones $CF_3COCH_3$ and $CFH_2COCH_3$, where $CH_3CO^+$ is the base peak and the $CF_3CO^+$ and $CFH_2CO^+$ ions possess about 10% relative intensity (8, 9).

## EXPERIMENTAL

A 5 l, three-necked flask equipped with a mechanical stirrer and a dry ice condenser was charged with 1 825 g (10 moles) of $CClF_2COCF_3$ (Allied Chemical Corporation) at −10°. Then 1 662 g (10 moles) of $(C_2H_5O)_3P$ (V.C. Chemical Company) was added at such a rate that the temperature was kept at −10°, followed by 1 l of 10% sulfuric acid. The mixture was stirred at ambient temperature for 16 h, after which it was heated under reflux for 5 h. The entire solution was then added dropwise to 6 l of concentrated $H_2SO_4$ and 2 600 g of $P_2O_5$ kept at 110° in a 12 l, three-necked flask. The effluent gases were condensed by means of a large, dry ice filled cold-finger head into a 2 l distilling flask. Distillation, using a 3

---

[1] Present address: Chemistry Department, University of Florida, Gainesville, Florida.

[2] Present address: Chemistry Department, University of California, Santa Barbara, California.

[3] We have duplicated the synthesis of 1-chloro-1,1,3,3-tetrafluoroacetone as described in ref. 4 and have found that a chromatographically pure sample of this compound boiled at 50° rather than at 57° as reported.

TABLE I

Mass spectrum of pentafluoroacetone

| $m/e$ | Relative abundance* | Probable positive ion |
|---|---|---|
| 12 | 21 | C |
| 13 | 26 | CH |
| 29 | 126 | CHO |
| 31 | 148 | CF |
| 32 | 102 | CFH |
| 50 | 108 | $CF_2$ |
| 51 | 1 000 | $CF_2H$ |
| 59 | 32 | $C_2FO$ |
| 69 | 482 | $CF_3$ |
| 78 | 86 | $C_2F_2O$ |
| 79 | 419 | $C_2F_2HO$ |
| 97 | 49 | $C_2F_3O$ |
| 100 | 11 | $C_2F_4$ |
| 101 | 104 | $C_2F_4H$ |
| 148 | 14 | $C_3F_5HO$ |

*$m/e$ peaks less than 1% of the peak at $m/e$ 51 have been omitted; no isotope corrections have been made, and the isotope peaks have been omitted.

ft vacuum-jacketed column packed with Heli-pak, produced 1 260 g (8.5 moles) of pentafluoroacetone, b.p. 12.5–13.5°. Analytical chromatography, using a 15 ft × $\frac{1}{4}$ in. outside diameter column packed with 33% Kel-F No. 3 oil on Chromosorb P, a helium flow rate of 100 cc/min, and ambient temperature, showed that the material was greater than 99.5% pure.

Its molecular weight, as determined by gas density, was 144 (calculated for $C_3HF_5O$: 148). The vapor-phase infrared spectrum exhibited principal absorptions at 3.34 (w), 5.59 (s), 7.33 (m), 7.41 (s), 7.68 (s), 8.13 (s), 8.42 (s), 8.65 (m) (shoulder), 9.09 (s), 9.98 (s), 11.60 (m), 13.50 (w), and 14.75 (w) $\mu$. The $^{19}F$ nuclear magnetic resonance spectrum showed a triplet centered at 76.7 p.p.m. (referred to $CFCl_3$) with a splitting of 6.2 c.p.s., and a doublet centered at 129.1 p.p.m. with a splitting of 52 c.p.s., each part of which was further split into a quadruplet with a separation of 6.2 c.p.s. The $^1H$ nuclear magnetic resonance spectrum exhibited a triplet centered at 5.45 $\tau$ relative to $CH_3CHO$, with a splitting of 52 c.p.s.

The photolysis of the ketone was carried out in the gas phase at 2 cm pressure in a 200 ml quartz reaction vessel kept at 140°. The ketone was taken to about 5% decomposition. A high-pressure mercury arc was employed, so that photolysis was mainly in the 3 130 Å region. The products were separated by low-temperature fractionation and analyzed by mass spectroscopy and vapor-phase chromatography. The fluorocarbons were analyzed on 2 ft and 15 ft columns of 3% squalane on 60–80 mesh alumina at 40°, with a helium flow rate of 60 cc/min.

## ACKNOWLEDGMENT

M. J. Perona and G. O. Pritchard thank the National Science Foundation for a grant-in-aid.

1. E. T. McBee, O. R. Pierce, H. W. Kilbourne, and E. R. Wilson. J. Am. Chem. Soc. **75**, 3152 (1953).
2. R. N. Haszeldine. J. Chem. Soc. 1273 (1954).
3. C. Woolf. *In* Encyclopedia of chemical technology. Vol. 9. John Wiley & Sons, Inc., New York. 1966. p. 755.
4. W. J. Middleton and R. V. Lindsey, Jr. J. Am. Chem. Soc. **86**, 4948 (1964).
5. J. Gordon and C. Woolf. U.S. Patent No. 2,917,546 (December 1959).
6. G. O. Pritchard and J. T. Bryant. J. Phys. Chem. **70**, 1441 (1966).
7. M. G. Bellas, O. P. Strausz, and H. E. Gunning. Can. J. Chem. **43**, 1022 (1965).
8. J. R. Majer. Advan. Fluorine Chem. **2**, 55 (1961).
9. G. O. Pritchard and R. L. Thommarson. J. Phys. Chem. **71**, 1674 (1967).

Received June 19, 1967.

Hynes Chemical Research Corporation,
Durham, North Carolina.

---

# The addition of "bromine fluoride" to norbornene[1]

F. H. Dean,[2] D. R. Marshall, E. W. Warnhoff, and F. L. M. Pattison

The addition of "BrF" to aliphatic (1) and alicyclic (2) systems has received considerable attention, particularly as a route to fluorinated steroids. In this note we report the addition of "BrF" to a simple bridged bicyclic system, with concomitant Wagner–Meerwein rearrangement.

Norbornene (I) was chosen as the simplest representative alkene of this type; also, it has been studied by Kwart and Kaplan (3) in the analogous addition reaction with molecular bromine. The addition of "BrF" ($N$-bromoacetamide and hydrogen fluoride in ether) to I produced three compounds

---

[1] Taken in part from the Ph.D. thesis of F. H. Dean.

[2] Present address: Ontario Research Foundation, Toronto, Ontario.