Anal. Calcd. for $C_{12}H_{16}N_4O_8$: C, 42.0; H, 4.65; N, 16.3. Found: C, 42.55; H, 5.03; N, 16.58.

In addition there was distilled 40 g. (80%) of the urethan 2-pyrrolidinoethyl pyrrolidine-1-carboxylate, b.p. 137–42° (3 mm.), $n^{20}D$ 1.4872. This product was identified by its infrared spectrum and by analysis of the picrate, m.p. 119–120°, crystallized from methanol.

Anal. Calcd. for $C_{17}H_{23}N_5O_9$: C, 46.3; H, 5.2; N, 15.8. Found: C, 46.44; H, 5.53; N, 15.7.

A Preparation of Primary Aliphatic Nitramines

LAWRENCE J. WINTERS, DAVID B. LEARN,[1] AND SHANTILAL C. DESAI

Department of Chemistry, Drexel Institute of Technology, Philadelphia, Pennsylvania

Received December 14, 1964

Primary aliphatic nitramines have most frequently been prepared by a four-step procedure: (1) acylation of the alkanamine to form the urethan; (2) nitration of the urethan; (3) ammonolysis of the N-nitrourethan to produce the ammonium salt of the nitramine; and (4) acidification of the salt to obtain the N-nitroalkanamine.[2,3]

Emmons and Freeman[4] have described an alkaline nitration method for the preparation of alkylnitramines using acetone cyanohydrin nitrate as the nitrating agent and an excess of an alkylamine. It is not possible to nitrate amines with branching on the α-carbon atom using this procedure.

We have devised a method[5] for the direct transformation of primary aliphatic amines[6] to the corresponding nitramines. This procedure involves the irreversible conversion of an amine to its conjugate base by *n*-butyllithium and subsequent nitration using ethyl nitrate as the nitrating agent. Primary, secondary,

$$RNH_2 \xrightarrow{n\text{-}C_4H_9Li} RNHLi \xrightarrow{C_2H_5ONO_2} RN(NO_2)Li \xrightarrow{H^+} RN(NO_2)H$$

and tertiary carbinylamines can be converted to the corresponding nitramine (*cf.* Table I). There are several advantages to this procedure. First, the preparation can be carried out as a one-step process. In addition, the method uses relatively simple equipment, employs readily available commercial reagents, and gives yields of product which are comparable to those obtained by other preparative routes.[2-4] Using this procedure, one can isolate the primary nitramine without conversion to an insoluble salt or secondary nitramine. The main disadvantage to this approach is that amines bearing functional groups reacting with *n*-butyllithium do not form nitramines. This procedure appears to complement the method of Emmons and Freeman[4] since it is not possible to convert secondary and tertiary carbinylamines using their approach and ours is limited to amines not having reactive functional groups.[7] It is evident that ethyl nitrate is

TABLE I

ALKALINE NITRATION OF AMINES

Nitramine	Solvent	Reaction temp.	Yield, %	Molar ratio, *n*-C_4H_9Li–RNH_2–$C_2H_5ONO_2$	B.p., °C. (mm.)
$CH_3N(NO_2)H$	Ether	Addition of reactants at Dry Ice temperature, then stirred at room temperature	35[a]	2:2:1[b,c]	80–85 (10)[d]
	Hexane	Dry Ice	22	2:1:1[b]	
i-$C_3H_7N(NO_2)H$	Hexane[e]	Dry Ice	44	2:1:1	
	Ether–hexane (2:1)	Dry Ice	58	2:1:1	
	Hexane	Dry Ice	40	2:1:1[f]	87–88 (10)[g]
	Hexane	Dry Ice	35	1:1:1[c]	
n-$C_4H_9N(NO_2)H$	Hexane	Dry Ice	49	2:1:1	
	Ether–hexane (2:1)	Dry Ice	30	2:1:1	92 (0.5)[h]
sec-$C_4H_9N(NO_2)H$	Hexane[e]	Dry Ice	43.7	2:1:1	110 (10)[i]
	Hexane	Dry Ice	45	3:1:1	
	Hexane	Steam refluxed	4.0	2:1:1	
	Ether	Addition of reactants at 0°, steam refluxed during stirring	15.5	2:1:1	
t-$C_4H_9N(NO_2)H$	Hexane	Dry Ice	37	2:1:1	
	Hexane	0° during *n*-C_4H_9Li addition, steam refluxed at other times	14	2:1:1	86–87 (10)[j]
n-$C_{10}H_{21}N(NO_2)H$[k]	Ether–hexane (2:1)	Dry Ice	46[l]	2:1:1	

[a] The aqueous layer was continuously extracted with ether for 20 hr. [b] Phenyllithium in ether was used in place of the *n*-butyllithium reagent. [c] The reactants were added to the reaction mixture in one step. [d] Lit.[2] b.p. 158° (766.3 mm.). [e] The hexane was distilled over lithium aluminum hydride. [f] The addition of ethyl nitrate was done rapidly. [g] B.p. 90–91° (10 mm.) is reported by M. J. C. A. Simon Thomas [*Rec. trav. chim.*, **9**, 77 (1890)]. [h] Lit.[4] b.p. 68–70° (0.05 mm.). [i] B.p. 106.2–106.7° (15 mm.) is reported by G. N. R. Smart and G. F. Wright [*Can. J. Res.*, **B26**, 290 (1948)]. [j] B.p. 94–95° (16 mm.) and 71° (0.6 mm.) are reported by J. Barrott, I. N. Denton, and A. H. Lamberton [*J. Chem. Soc.*, 1998 (1963)]. [k] Crystallized twice from hexane, m.p. 38–38.8°. *Anal.* Calcd. for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.62; H, 11.08; N, 14.01. [l] Based on the weight of crude product obtained.

(1) Undergraduate National Science Foundation research participant, 1963–1964.

(2) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 343 (1888).

(3) H. M. Curry and J. P. Mason, *J. Am. Chem. Soc.*, **73**, 5043 (1951).

(4) W. D. Emmons and J. P. Freeman, *ibid.*, **77**, 4387 (1955).

(5) Similar methods are well known for the preparation of aromatic nitramines: W. N. White, *et al.*, *J. Org. Chem.*, **26**, 4124 (1961).

(6) The direct nitration of aliphatic amines has been reported using nitryl fluoride, a corrosive gas, as the nitrating agent: H. C. Mandell, Jr., U. S. Patent 3,071,438 (1962); *Chem. Abstr.*, **59**, 447 (1963).

(7) The authors are grateful to the referee for making these observations.

better than acetone cyanohydrin nitrate as an nitrating agent for sterically hindered amines.

The reaction was studied to determine the optimum conditions for obtaining the maximum yield of product. In certain instances (*cf.* Table I), higher yields were obtained using ether or an ether–hexane mixture (2:1 by volume) as the solvent rather than pure hexane. Low temperatures and alternate additions of *n*-butyllithium and ethyl nitrate seemed to increase the yields of product. Maximum yields were obtained when the ratio of reactants of *n*-butyllithium–amine–ethyl nitrate was 2:1:1.

Experimental

Materials.—The hexane was mechanically stirred overnight with concentrated sulfuric acid, washed with aqueous sodium carbonate and water, and finally dried over sodium. For some of the reactions, the hexane was dried further by distillation over lithium aluminum hydride, but this seemed to make very little difference in the resultant yield. The ethyl ether was dried over sodium, and the liquid amines were either stored over sodium hydroxide pellets or distilled over calcium oxide to remove traces of water. The *n*-butyllithium reagent was a 15% solution in hexane (Foote Mineral Co., New Johnsville, Tenn.). Phenyllithium was prepared by treating bromobenzene with lithium in dry ether.[8]

Procedure.—The basic procedure for the preparation of the primary aliphatic nitramines is outlined as follows. The solvent (200–300 ml.) was placed in a flask equipped with a mechanical stirrer, Dry Ice condenser, and two dropping funnels containing ethyl nitrate and *n*-butyllithium reagent. The reaction mixture was vigorously stirred while immersed in a Dry Ice–acetone bath and was kept under a dry nitrogen atmosphere. The amine (0.33 mole) was added to the flask followed by rapid addition of 0.33 mole of the *n*-butyllithium reagent. Then 0.17 mole of ethyl nitrate was added dropwise during a 1-hr. period and the reaction mixture was stirred for an additional hour. Two more addition steps followed, both consisting of a rapid addition of 0.17 mole of *n*-butyllithium reagent and a dropwise addition of 0.083 mole of ethyl nitrate over a period of 0.5 hr., after which the reaction was stirred for an additional 0.5 hr. After the reaction mixture was allowed to come to room temperature, sufficient water was added to dissolve the lithium salt of the nitramine and any other solid material. The water layer was separated from the hexane layer, acidified at 0° to pH 1 with hydrochloric acid, and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and filtered and the solvent was removed by distillation. The crude product was distilled at 10-mm. pressure or less (see Table I for yields of purified product).

Acknowledgment.—The elemental analysis was performed by A. Bernhardt, Mülheim (Ruhr), Germany. We thank the National Science Foundation for support of D. B. L. and Drexel Institute of Technology for a faculty research grant.

(8) H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 286 (1954).

Perfluorobiacetyl from the Oxidation of Perhalobutenes[1]

LEONARD O. MOORE AND JARED W. CLARK

Research and Development Department, Union Carbide Corporation, Chemicals Division, South Charleston, West Virginia

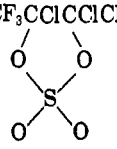
Received May 16, 1963

Only a limited number of perfluoro α,β-diketones have been described in the literature. The first member, perfluorobiacetyl (PFBA), has not been described before, although several attempts have been made in this direction.[2-4] Tucker and Whittle[5] recently indicated that they thought the reason PFBA had not been observed in the hexafluoroacetone photolysis was its instability. The only presently known examples of fluorinated open-chain α,β-diketones are those in which R of R–CO–CO–R is perfluoropropyl,[6] perfluoroisopropyl,[7] and octafluorobutyl.[6] The cyclic diketone, perfluorocyclobutane-1,2-dione, has also been described.[8] The straight-chain compounds were prepared by the condensation of polyfluoroacyl chlorides in the presence of nickel carbonyl to give enediol diesters which pyrolyzed to the α,β-diketones,[6] the perfluoroisopropyl compound was made by the addition of oxalyl fluoride to perfluoropropene catalyzed by fluoride ion,[7] and the cyclic member of this series was made by the hydrolysis of 1,2-dimethoxyhexafluorocyclobutane.[8]

We have now synthesized the first and simplest member of the series by a new and relatively simple method. PFBA was obtained from 2,3-disubstituted 1,1,1,4,4,4-hexafluoro-2-butenes and from perfluoro-2-butyne by oxidation with chromium trioxide in sulfuric acid. The best synthesis utilized 2,3-dichloro-1,1,1,-4,4,4-hexafluoro-2-butene which is the highest boiling of the starting materials tried and gave the best yield, about 35%. The three other compounds examined were low-boiling materials and were only partly oxidized when passed through a solution of chromium trioxide in sulfuric acid at 50°.

$$CF_3CCl{=}CClCF_3 + CrO_3 + H_2SO_4 \longrightarrow$$

$$CF_3COCOCF_3 + CF_3COCl + CF_3CClCClCF_3 + Cl_2$$



PFBA is a deep yellow liquid boiling at 20° and freezing at −20°. This boiling point is 68° lower than that of biacetyl, but such a difference is not unique; most perfluorinated compounds have a boiling point lower than their hydrocarbon analogs. Notably, the perfluorinated carbonyl compounds of two, three, four, and eight carbon atoms all boil about 70–80° lower than their hydrocarbon equivalents. The ultraviolet spectrum of PFBA is very close to that of biacetyl, having maxima at 422 mμ (ε 13.9) and 443 mμ (ε 13.0) and shoulders at 290 mμ (ε 19.4), 303 (ε 14.9), 415 (ε 13.7), and 450 (ε 11.8). Biacetyl has maxima at 280 and 420 mμ and a shoulder at 440 mμ. The infrared spectrum is, as expected, different from that of biacetyl, and has

(1) Presented at the 2nd International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1962.

(2) R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

(3) R. N. Haszeldine, *Nature*, **168**, 1028 (1951); E. T. McBee, O. R. Pierce, H. W. Kilbourne, and J. A. Barone, *J. Am. Chem. Soc.*, **75**, 4090 (1953).

(4) S. J. W. Price and K. O. Kutschke, *Can. J. Chem.*, **38**, 2128 (1960), and references cited therein.

(5) B. G. Tucker and E. Whittle, *Proc. Chem. Soc.*, 93 (1963).

(6) J. J. Drysdale and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 511 (1960); J. J. Drysdale (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,012,-069 (Dec. 5, 1961).

(7) R. D. Smith, F. S. Fawcett, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4285 (1962).

(8) D. C. England, *ibid.*, **83**, 2205 (1961); E. I. du Pont de Nemours and Co. (by D. C. England), British Patent 873,222 (July 19, 1961).