

the change in the heats of formation cannot be accounted for by the values reported in the literature for the molecular configuration of the paraffin chain. This leads to the conclusion that there is an interaction between the iso-alkyl group and the fluoronitramine group. The difference between the heats of formation of the normal and *sec*-butyl-*N*-fluoronitramines is in the range of differences reported for many other isomeric compounds (Table III). However, there is a "jump" in the heat of formation from the *sec*- to the *tert*-butyl-*N*-fluoronitramine. The difference between these isomers is unusually high, but is supported by decomposition rate studies. The *n*- and *sec*-butyl-*N*-fluoronitramines show approximately the same decomposition rate ( $0.8 \cdot 10^{-4} \text{ sec}^{-1}$ ); the tertiary compound has a twenty times higher decomposition rate ( $24 \cdot 10^{-4} \text{ sec}^{-1}$ ) (6).

It is assumed that branching of the butyl chain introduces strain into the molecule by steric hindrance and electronic configuration.

#### ACKNOWLEDGMENT

This investigation was supported by the Bureau of Naval Weapons, Department of the Navy, through Task Assignment RMMP-22-153/286-1/R001-06-01. The authors thank Manfred Cziesla for fruitful discussions during the course of this investigation and acknowledge the support given by J. G. Tuono and G. Tesi.

#### LITERATURE CITED

- (1) Baroody, E.E., Wynne, J., Zimmer, M.F., U.S. Naval Propellant Plant, *NavWeps Rept.* 8686, Tech. Rept. 154, 1964.

- (2) Cox, J.D., Head, A.J., *Trans. Faraday Soc.* 58, 1839-45, (1962).  
 (3) Crankankas, V., Aerojet-General Corp. *Rept. No.* 0235-01-7, Quarterly Report, 15 July 1960 (confidential).  
 (4) Good, W.D., Douslin, D.W., McCullough, J.P., *J. Phys. Chem.* 67, 1312-4 (1963).  
 (5) Good, W.D., Scott, D.W., Waddington, G., *Ibid.*, 68, 1080 (1956).  
 (6) Graff, M., Cziesla, M., "Study of the Decomposition Mechanism of *N*-Fluoro-*N*-nitrobutylamines," U.S. Naval Propellant Plant, 1965, unpublished data.  
 (7) Graff, M., *et al.*, *NavWeps Rept.* 8571, Tech. Rept. 147, 5 June 1964 (confidential).  
 (8) Hammond, J.E., Kordite Corp., Macedon, N. Y., private communication.  
 (9) "Handbook of Chemistry," N. A. Lang, Ed., 10th ed., McGraw-Hill, New York, 1961.  
 (10) "Handbook of Chemistry and Physics," 43rd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.  
 (11) Ketelaar, J.A., "Chemical Constitution," p. 191, Elsevier Publishing Co., London, 1953.  
 (12) Klages, F., *Chem. Ber.* 82, 358, (1948).  
 (13) Lehmann, H., Ruschitzky, E., *Chem. Tech.* 16, 18, (1964).  
 (14) Marantz, Sidney, National Bureau of Standards, Washington, D. C., private communication.  
 (15) Rossini, F.D., "Experimental Thermochemistry," Vol. I, pp. 90, 107, Interscience, New York, 1962.  
 (16) Skinner, H.A., *Ibid.*, Vol. II, pp. 25-8, 1962.  
 (17) Wilkins, R.L., "Theoretical Evaluation of Chemical Propellants," C.N. Besserer, F.E. Nixon, Eds., Prentice Hall, Englewood, N.J., 1963.  
 (18) Zimmer, M.F., Baroody, E.E., Schwartz, M., McAllister, M.P., *J. CHEM. ENG. DATA* 9, 527 (1964).

RECEIVED for review December 6, 1965. Accepted June 22, 1966. 3rd International Symposium on Fluorine Chemistry, Aug./Sept. 1965. Munich, W. Germany.

## Alkyl Ethers

D. V. LOPIEKES

Boston Laboratory, Monsanto Research Corp., Everett, Mass.




A SERIES of ethers was obtained by the reaction of phenylmagnesium bromide, prepared commercially by the Arapahoe Chemical Co. as a 3*M* solution, with acetals above 100° C. in xylene according to a procedure of Kaye and Kogon (1). Table I summarizes the yield, boiling point, refractive index, and elemental analysis of the compounds prepared. The infrared spectra were consistent in each instance with the desired structure.

#### LITERATURE CITED

- (1) Kaye, I.A., Kogon, I.V., *J. Am. Chem. Soc.* 73, 4893 (1951).

RECEIVED for review January 14, 1966. Accepted April 19, 1966. Work supported by the U. S. Army Biological Laboratories, Fort Detrick, Md. Elemental analysis performed by Carol K. Fitz, Needham Heights, Mass.

Table I.  $\text{C}_6\text{H}_5-\text{CH}(\text{OR})\text{CH}_2-\text{R}'$

R	R'	B.P. <sup>a</sup>		Yield, %	$n_D^{20}$	Formula	Analysis					
		° C.	Mm.				Carbon		Hydrogen		Nitrogen	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{C}_2\text{H}_5-$		70-72	0.14	47	1.5125 <sup>25</sup>	$\text{C}_{14}\text{H}_{21}\text{NO}$	77.0	77.5	9.7	9.4	6.3	6.4
$\text{C}_2\text{H}_5-$	$-\text{N}(\text{C}_2\text{H}_5)_2$	77-79	8.0	68	1.4872 <sup>25</sup>	$\text{C}_{14}\text{H}_{23}\text{NO}$	75.9	75.9	10.5	10.5	6.3	6.5
$\text{C}_2\text{H}_5-$	$-\text{OC}_6\text{H}_5$	106	0.04	40	1.5457 <sup>25</sup>	$\text{C}_{16}\text{H}_{18}\text{O}_2$	79.3	79.5	7.5	7.6	...	...
$\text{C}_2\text{H}_5-$		82-86	0.05 <sup>b</sup>	50	1.5112 <sup>20</sup>	$\text{C}_{15}\text{H}_{23}\text{NO}$	77.2	77.0	9.9	10.0	6.0	5.9
$\text{C}_2\text{H}_5-$		143-45	10.3 <sup>c</sup>	50	1.5070 <sup>25</sup>	$\text{C}_{14}\text{H}_{21}\text{NO}_2$	71.4	71.3	9.0	8.8	6.0	5.9

<sup>a</sup> Boiling points uncorrected. <sup>b</sup> Kaye and Kogon reported b.p. 135-47° C./9 mm.; yield, 62%. <sup>c</sup> Kaye and Kogon reported b.p. 134-36° C./10 mm.; yield, 23%.