Alkylation of Benzene with Straight-Chain Olefins. IV. Effect of the Counterion on the Isomerization of Secondary Carbonium Ions

HUSNI R. ALUL* AND GILBERT J. MCEWAN

Detergent and Phosphate Research and Development Department, Monsanto Industrial Chemicals Company, St. Louis, Missouri 63166

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1-Dodecene and *trans*-6-dodecene alkylate benzene in the presence of anhydrous hydrogen fluoride at 0 and 55° to give different isomer distributions of phenyldodecanes. Lower olefins, C_{10} and C_8, behave in a similar manner, but 1-hexene and *trans*-3-hexene afford similar amounts of 2- and 3-phenylhexanes at 0°. Addition of BF_3 to HF alters the isomer distribution significantly and raises the amount of the 2 isomer at the expense of the internal ones. At 35° or higher alkylation in the presence of HF-BF_3 is accompanied by isomerization of the products to a certain equilibrium distribution that results in the same isomer distribution regardless of the position of the double bond in the starting olefin. This product isomerization is suppressed at 0° and the isomer distribution of the products depends on the position of the double bond in the olefin. Experimental evidence is presented which shows that the change in the isomer distribution due to the addition of BF_3 at 0°, *i.e.*, in the absence of product isomerization, is due to the introduction of BF_4^- ions in the ion pairs rather than to the rise in the acidity of the system.

Alkylation of benzene with a long-chain olefin in the presence of strong Friedel–Crafts catalysts such aluminum chloride affords all the isomeric phenylalkanes except the 1 isomer.[1] Friedel–Crafts alkylations have long been known to be accompanied by isomerization, disproportionation, and transalkylation.[2-5] The phenylalkanes initially formed undergo extensive isomerization to a certain equilibrium distribution that is different from the isomer distribution obtained in the absence of product isomerization. The reaction in the presence of product isomerization is thermodynamically controlled and the isomer distribution of the product is the same regardless of the position of the double bond in the starting olefin.[6,7] Consequently both 1-dodecene and *trans*-6-dodecene afford nearly identical isomer distributions including about 32% 2-phenyldodecane and 31% 5 and 6 isomers. We define this as a distribution ratio of 32:31. Product isomerization which accompanies the alkylation reaction can be suppressed by carrying out the reaction at 0° or by using a weaker catalyst such as aluminum chloride–nitromethane. Under these conditions the isomer distribution of the product is kinetically controlled[7] and depends on the position of the double bond in the olefin.[6] Thus 1-dodecene shows a significantly higher distribution ratio, 44:20, while the internal olefin is very much lower, 18:53.

Alkylation in the presence of anhydrous hydrogen fluoride is not accompanied by product isomerization even at 55°. It is similar to the reaction with aluminum chloride at 0° in that terminal and internal olefins afford different isomer distributions.[8] However, the isomer distribution of the product from the reaction with HF is significantly different from that with $AlCl_3$ even though both are carried out under conditions which do not permit product isomerization. Thus at 0–5° 1-dodecene affords the ratio 18.5:47.7 in the presence of HF and 44.0:19.7 in the presence of $AlCl_3$.

From the point of view of their catalytic activity in these reactions the most important differences between HF and $AlCl_3 \cdot HCl$ are (a) the difference in their acidity, and (b) the difference in the mobility of F^- and $AlCl_4^-$ ions. The Hammett acidity function, H_0, for anhydrous HF is -10.8 and that for $AlCl_3 \cdot HCl$ is about -16 which makes the latter a much stronger acid. The acidity of hydrogen fluoride, however, can be varied over a very wide range (six powers of 10) by addition of certain Lewis acids (coacids) such as BF_3, NbF_5, or SbF_5 which raise the acidity of the solvent by setting up the equilibrium[9]

$$BF_3 + 2HF \rightleftharpoons H_2F^+ + BF_4^-$$

Since the ionic product of anhydrous hydrofluoric acid is only 2×10^{-10} and the equilibrium constant for the reaction

$$BF_4^- \rightleftharpoons BF_3 + F^-$$

is between 5×10^{-3} and 2.5×10^{-7} addition of BF_3 to HF converts fluoride ions into tetrafluoroborate ions.[10-12] This makes the system HF–BF_3 particularly useful for this study since both the acidity and the counterion, or gegenion, of the ion pair can be varied over a wide range and the experimental conditions can be controlled such that alkylation occurs in the absence of product isomerization.

Results

Alkylation of benzene with 1-dodecene in the presence of anhydrous hydrogen fluoride at 0° affords a product with a distribution ratio of 18.5:47.7. Addition of gaseous BF_3 to the reaction mixture results in a substantial rise in the amount of the 2-phenyldodecane and a corresponding decrease in the internal isomers. Thus a 5% solution of BF_3 in HF at the same temperature raises the distribution ratio to 41.0:26.8. This effect appears to be a function of the amount of BF_3

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(1) R. D. Swisher, E. F. Kaelble, and S. K. Liu, *J. Org. Chem.*, **26**, 4066 (1961).

(2) D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, **75**, 2411 (1953).

(3) D. A. McCaulay in "Friedel–Crafts and Related Reactions," Vol. II, G. Olah, Ed., Interscience, New York, N. Y., 1964, p 1049.

(4) H. C. Brown and J. H. Ungk, *J. Amer. Chem. Soc.*, **78**, 2182 (1956).

(5) A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

(6) H. R. Alul, *J. Org. Chem.*, **33**, 1522 (1968).

(7) C. D. Nenitzescu, *Rev. Roum. Chim.*, **9**, 5 (1964).

(8) H. R. Alul and G. J. McEwan, *J. Org. Chem.*, **32**, 3365 (1967).

(9) M. Stacey, J. C. Tatlow, and A. G. Sharpe, *Advan. Fluorine Chem.*, **1**, 75 (1960).

(10) M. Kilpatrick and F. E. Luborsky, *J. Amer. Chem. Soc.*, **76**, 5865 (1954).

(11) M. Kilpatrick and F. E. Luborsky, *ibid.*, **76**, 5863 (1954).

(12) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

in HF as can be seen from Table I. The same type of effect is also observed with the internal olefin, *trans*-6-dodecene, where addition of 5% BF_3 raises the distribution ratio from 10.6:58.6 to 24.7:43.6. A sample of 2-phenyldecane added along with the olefin to detect any product isomerization showed no isomerization to the internal phenyldecanes indicating the absence of any product isomerization as well. At 35°, however, the 2-phenyldecane tracer showed extensive isomerization to the internal isomers and the distribution ratio of the product, phenyldodecane, fell to 33.5:32.5, which is similar to that obtained with $AlCl_3 \cdot HCl$ at the same temperature.[7] Alkylation in the presence of a 0.5 *M* solution of KBF_4 in HF raises the 2-phenyl content of the product by a small but measurable amount (from 18.5 to 22.5%) as does also alkylation in the presence of KF (Table I).

TABLE I

ALKYLATION OF BENZENE WITH OLEFINS IN THE PRESENCE OF HF–BF_3 AT 0–5°

Olefin	% BF_3 in HF	%			
		2-Phenyl	3-Phenyl	4-Phenyl	5- + 6-Phenyl
1-Dodecene	0	18.5	15.5	18.3	47.7
	1.0	22.5	16.7	16.0	44.8
	2.5	35.0	19.4	14.7	30.9
	4.0	39.7	20.3	13.8	26.2
	5.0	41.0	18.4	13.8	26.8
		100.0[a]			
b	5.0	33.5	17.8	16.2	32.5
		37.8[a]	25.3	17.4	19.5
c	2.1 (NaF)	21.6	17.2	16.3	44.9
d	6.3 (KBF_4)	22.5	17.0	16.9	43.6
6-Dodecene	0	10.6	12.7	17.9	58.6
	5.0	24.7	15.8	15.9	43.6
1-Decene	0	22.6	21.8	23.4	32.2
	5	41.7	22.1	16.4	19.8
5-Decene	0	16.2	19.3	25.5	39.0
	5.0	29.1	20.7	20.3	29.9
1-Octene	0	32.1	32.4	35.5	
	5.0	47.3	28.3	24.4	
4 Octene	0	28.5	32.4	39.1	
	0	40.0	29.2	30.8	
1-Hexene	0	57.3	42.7		
	5	63.5	36.5		
e	0	62.6	37.4		
3-Hexene	0	57.0	43.0		
	5	61.0	39.0		
e	0	59.8	40.2		

[a] Analysis of the added 2-phenyldecane to detect product isomerization. [b] Reaction was carried out at 35–40°. [c] Sodium fluoride instead of BF_3 was used in this experiment and it amounts to 0.5 *M*. [d] Potassium tetrafluoroborate was used instead of BF_3 and it amounts to 0.5 *M*. [e] Reaction was carried out at 155°.

Alkylation of benzene with C_{10} or C_8 olefins in the presence of anhydrous hydrogen fluoride is similar to that with the dodecenes in that the position of the double bond is a factor in the isomer distribution of the product. Table I shows that the amount of the 2-phenylalkane is greater for the terminal olefins than for the internal ones. Also addition of BF_3 to HF results in a substantial change in the isomer distribution of the products from both types of olefins in favor of greater formation of the 2-phenylalkane isomer at the expense of the internal ones.

Both 1-hexene and *trans*-3-hexene alkylate benzene in the presence of HF at 0° to afford, within the experimental error, similar amounts of 2- and 3-phenylhexanes. This indicates that in contrast to the higher olefins the position of the double bond is not a factor in the isomer distribution of the product. However, at 55° a slight difference between the two olefins appears with the α olefin producing slightly greater amounts of the 2 isomer. A similar result was obtained with HF–BF_3 or recycled aluminum chloride (Table II).

TABLE II

ALKYLATION OF BENZENE WITH 1- AND 3-HEXENES IN THE PRESENCE OF RECYCLED $AlCl_3$[a]

Olefin	Temp, °C	%	
		2-Phenyl	3-Phenyl
1-Hexene	5	67.2	32.8
3-Hexene	5	62.5	37.5
1-Hexene	35–40	68.7	31.3
3-Hexene	35–40	65.9	34.1

[a] Recycled aluminum chloride was used to prevent product isomerization.[6]

In the presence of HF alone the yields of the monoalkylbenzenes were ~90%. Only the hexenes gave a small amount (2%) of dialkylbenzene. Addition of BF_3 resulted in a rise in the amount of dialkylbenzene which increased with decreasing chain length and amounted to 25% of the yield in the case of the hexenes. Under these conditions the yield of phenylhexanes dropped to 62%.

Discussion

The generally accepted mechanism for Friedel–Crafts alkylations involves interaction of the olefin with the catalyst to form a carbonium ion, the corresponding ion pair, or a polarized complex. This undergoes rapid isomerization in varying degrees and finally attacks benzene in what is considered to be the rate-determining step, to form the products.[13] In the alkylation of benzene with a long-chain olefin such as 1-dodecene the alkylation step is too fast to permit the intermediate secondary carbonium ions to come to equilibrium prior to their attack on benzene.[6,8] The present data indicate that shortening the alkyl chain to C_{10} or C_8 is not sufficient to bring about the equilibrium condition among the carbonium ions before the alkylation step of the reaction sequence. Consequently, the α olefins 1-decene and 1-octene afford different isomer distributions from the corresponding internal ones, *trans*-5-decene and *trans*-4-octene. With the hexenes, however, the secondary carbonium ions apparently do come to equilibrium at 0° and the isomerization reaction

$$\mathrm{C{-}C{-}C{-}C{-}\overset{+}{C}{-}C} \rightleftharpoons \mathrm{C{-}C{-}C{-}\overset{+}{C}{-}C{-}C}$$

is, therefore fast compared with the alkylation step itself. Consequently both 1-hexene and *trans*-3-hexene afford similar isomer distributions. This condition of equilibrium among the hexyl carbonium ions appears to be only barely reached since at 55° the two isomeric olefins no longer afford the same isomer distribution. The difference between them, though small, is real and

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(13) S. H. Patinkin and B. S. Friedman in ref 3, Chapter 14, p 3.

reproducible.[14] It is also obtained with recycled aluminum chloride both at 5 and 35° (Table II).

Addition of BF_3 to HF at 0° alters the isomer distributions of all of the products and results in a substantial rise in the amount of the 2 isomer at the expense of the internal ones. Boron trifluoride increases the acidity of the system by shifting the equilibrium toward the formation of H_2F^+. The present data indicate that the rise in acidity is not responsible for the change in the isomerization across the chain or the substantial increase in the 2-phenyl content of the product, for, if this were so, then a decrease in acidity should be expected to have the opposite effect. Alkali metal fluorides behave as bases in HF and are completely ionic.[16] A 0.5 M solution of NaF in HF decreases the Hammett acidity function, H_0, from -10.8 to -8.6.[12] Alkylation of benzene with 1-dodecene in the presence of a 0.5 M NaF in HF resulted in an increase in the 2-phenyl content of the product from 18.5 to 21.6%. Therefore, decreasing the acidity of the catalyst did not result in a corresponding decrease in the 2-phenyl content of the product as would be expected had the original change in the isomer distribution been due to the increase in the acidity of the system brought about by addition of BF_3 to HF.

The absence of any effect for the acidity on the isomerization of the intermediate carbonium ions was also demonstrated for aluminum chloride alkylations. It is well known that in $AlCl_3$, H_2SO_4, and other acid-catalyzed alkylations, strong bases are produced which gradually destroy the catalyst.[17,18] Repeated alkylations of benzene with 1-dodecene in the presence of the same $AlCl_3$ catalyst phase were carried out at 0–5° until the catalyst became too weak to bring about complete alkylation and large amounts of the α olefin appeared in the product (seven alkylations). The isomer distributions of all the products from all of these reactions remained essentially the same with a distribution ratio of 43:20. Since 0.5 M NaF in HF, which has H_0 -8.6, is an effective alkylation catalyst the acidity of the last recycled $AlCl_3$ must have fallen below this level. Therefore, in this series of experiments the acidity was gradually decreased from H_0 -16 to below -8.6 without any visible effect on the isomer distribution of the product. The same result was also obtained in the presence of NaCl which acts as a base toward $AlCl_3$.[19] Thus alkylation with a catalyst that contained a mixture of recycled $AlCl_3$ plus NaCl and the same recycled catalyst plus fresh $AlCl_3$ afforded the same isomer distribution in spite of the large difference in the acidity of the two catalyst systems.

As was mentioned above, addition of BF_3 to HF increases the amount of the 2 isomer at the expense of the internal ones. This is more readily seen for the α olefins where the proton enters the alkylating agent near the end of the chain. Thus 1-decene affords the ratio 22.6:32.2 in the presence of HF and the ratio 41.7:19.8 in the presence of HF–BF_3. In other words, there is a tendency for the positive charge of the ion pair to remain near the end of the chain. This is also true of the other olefins and indicates that addition of BF_3 slows down the isomerization reaction of the intermediate carbonium ions relative to their rates of alkylation of benzene. This can also be seen from the fact that 1-dodecene affords 18.5% 2 isomer in the presence of HF and 41.0% in the presence of HF–BF_3. The slowing of the isomerization across the chain causes the intermediate ions to be farther away from the equilibrium position in the presence of HF–BF_3 than in the presence of HF alone.[20]

Studies on the reaction

$$BF_4^- \rightleftharpoons F^- + BF_3$$

in HF show that the equilibrium is largely toward the formation of the tetrafluoroborate ion.[11,12] The present data is in accord with the suggestion that the slowing of the isomerization reaction along the chain of an α olefin is due to the replacement of fluoride ions by tetrafluoroborate ions. The great mobility of F^- in HF solution is well known and Kilpatrick and Luborsky have demonstrated that addition of BF_3 to the potassium fluoride solution in HF results in a drop in conductivity owing to the replacement of solvated fluoride ions by the less mobile tetrafluoroborate ions.[11,21] Since the ions exist as ion pairs the negative ion must move along with the positive charge as it moves across the chain. This is in agreement with the behavior of KBF_4 which has been shown to be completely ionic in HF. As would be expected, however, its effect on the isomer distribution is not so large as that of BF_3 since in the latter case the fluoride ion is replaced by the tetrafluoroborate ion while addition of KBF_4 leaves the concentration of the fluoride ion essentially the same. A much larger effect was obtained by alkylation in the presence of HF–BF_3–KBF_4 where the distribution ratio from 1-dodecene rose to 39.0:27.8. Since KBF_4 acts as a base toward HBF_4[22] it was possible to alkylate with it at 55° without interference from product isomerization.

Finally, examination of Table I reveals that addition of BF_3 results in an increase in the amount of the 2 isomer from both types of olefins at the expense of the internal ones. In other words, there is a shift in the distribution of the intermediate carbonium ions toward greater formation of the 2 ion. Thus 5-decene affords the ratio 16.2:39.0 in the presence of HF and the ratio 29.1:29.9 in the presence of HF–BF_3. This can also

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[14] *Cf.* F. Asinger, B. Fell, H. Verbeek, and J. Fernandez-Bustillo, *Erdöl Kohle Chem.*, **11**, 786 (1967). These authors report that, in the alkylation of benzene with isomeric *n*-heptenes in the presence of HF or H_2SO_4, they obtained the same isomer distribution regardless of the position of the double bond in the starting olefin, concentration of the acid, mode of addition of the reactants, or temperature of the reaction. However, they were working between 0 and −30°. On the other hand, Kelly and Lee obtained results in hydride transfer reactions with 4-methyl-2-pentene and 4-methyl-1-pentene which led them to suggest that an appreciable time is required for a series of hydride shifts leading to the formation of the *tert*-carbonium ion structure.[15]

[15] J. T. Kelly and R. J. Lee, *Ind. Eng. Chem.*, **47**, 757 (1955).

[16] K. Fredenhagen, *Z. Anorg. Chem.*, **242**, 23 (1939); K. Fredenhagen and G. Cadenbach, *Z. Physik, Chem.*, **146**, 245 (1930).

[17] G. A. Olah and M. W. Meyer in "Friedel-Crafts and Related Reactions," Vol. I, George Olah, Ed., Interscience, New York, N. Y., 1963, p 736.

[18] N. C. Deno in "Progress in "Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., R. W. Taft, Ed., Interscience, New York, N. Y., 1964, p 141.

[19] F. H. Blunk and D. R. Carmody, *Ind. Eng. Chem.*, **40**, 2072 (1948).

[20] Although the isomer distribution of the phenylalkanes is not expected to correspond exactly to the actual concentration of the intermediate carbonium ions owing to differences in the rates of their alkylation of benzene, nevertheless, it is reasonable to assume that differences in the isomer distributions reflect differences in the concentrations of the intermediate ions. When the same isomer distribution is obtained regardless of the position of the double bond in the chain then the intermediate ions must have attained the equilibrium condition.[8]

[21] M. Kilpatrick and F. E. Luborsky, *J. Amer. Chem. Soc.*, **75**, 577 (1953).

[22] H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 235 (1966).

be readily explained by the effect of replacing the F^- ions by the larger BF_4^- ions in the ion pairs. In the 2-alkyl carbonium ions the positive charge is located near the end of the chain which permits more efficient solvation by the catalyst and a closer approach by the BF_4^- ions. As the charge enters the middle of the chain, the ion is more efficiently shielded from the BF_4^- ions by its two alkyl groups. This results in slightly greater stability for the 2-alkyl carbonium ions. In addition, evidence has previously been obtained which suggests that the 2-carbonium ion reacts faster with benzene than the internal ones.[6] Since the proton enters the alkylating agent at the center of the chain, which is only two carbon atoms away from the 2 position, this effect combines with the first one to raise the amount of the 2 isomer.

Experimental Section

Materials and Apparatus.—All of the 1-alkenes were obtained from the Aldrich Chemical Co. and the internal olefins were obtained from Farchan Research Laboratories, Cleveland, Ohio. Benzene was dried by azeotropic distillation and anhydrous aluminum chloride was Allied Chemical reagent grade. Anhydrous hydrogen fluoride and gaseous boron trifluoride were obtained from the Matheson Co. and used as received. 2-Phenyldecane was synthesized from acetophenone and *n*-octylmagnesium bromide (Grignard reaction). The tertiary alcohol was dehydrated over potassium bisulfate, and the olefin was hydrogenated to the phenyldecane with palladium on charcoal (5%). The product was about 97% pure as established by glc analysis.

The alkylation reactions were carried out in a 2-l. stainless steel reactor equipped with agitator, thermocouple, cooling coil, pressure gage, and various inlet ports for introducing catalyst and olefin, sampling the reaction mixture, venting the apparatus, and withdrawing the products. All the inlets were provided with stainless steel valves. Strict safety precautions were followed to avoid any contact with liquid or gaseous HF or BF_3.

General Procedure of Alkylation.—Anhydrous benzene (3.9 mol) was charged to the reactor and cooled to 5 to 7° with ice water circulated through the cooling coil. Anhydrous hydrogen fluoride (4 mol), cooled to about −30° with Dry Ice, was then added. All the valves were then closed except the venting valve which was connected through a Tygon tube to a BF_3 lecture bottle which rested on a balance. The calculated amount of BF_3 was then introduced, the valve was closed, and agitation was started. (For alkylations with HF only the BF_3 step was eliminated.) When the temperature reached 0–5°, 0.4 mol of the α olefin in 1 mol of benzene was pumped into the reactor over a 10-min period, using a microbellows pump (Research Appliance Co.). The reaction mixture was aged for 10 min at the same temperature, after which time it was settled for 1 hr to allow separation of the two phases. The catalyst was then drained onto crushed ice, neutralized, and discarded. The alkylate layer was quenched with ice and most of the benzene was removed under suction. The crude alkylbenzene was examined by glc using a Varian Aerograph Model 1800 equipped with an Infotronics electronic integrator. The stainless steel column was 150 ft. × 0.01 in. and was coated with silicon OV7. The crude products were then distilled and the material boiling in the range of the arylalkane was collected. In the presence of HF alone the yields were 87–91% of the theoretical amount. With HF–BF_3 they were 62, 70, and 77% for the C_6, C_8, and C_{10} alkylbenzenes, respectively. After removal of the phenylhexanes, distillation of the residue continued and a fraction boiling at 113–126° (2 mm) was collected (25%). This is close to the boiling point of dodecylbenzene.[8] Its ir spectrum showed it to be primarily dialkylbenzene (12.1 and 12.65 μ). The residues from the alkylations of the higher olefins also showed these bands indicating dialkylation of benzene as a side reaction.

The same procedure was followed for the alkylation of benzene with the internal olefins but the scale of the experiments was only half that of the α olefins.

Registry No.—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-13-5; 1-decene, 872-05-9; *trans*-5-decene, 7433-56-9; 1-octene, 111-66-0; *trans*-4-octene, 14850238; 1-hexene, 592-41-6; *trans*-3-hexene, 13269-52-8.

Radical Reactions of Tetrafluorohydrazine. Preparation of Bis(difluoramino)alkanols and Nitrates[1]

SAMUEL F. REED, JR.,* AND R. D. SHOULTS

Rohm and Haas Company, Research Laboratories, Spring House, Pennsylvania 19477

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The synthesis of difluoramino-substituted alkanols has been accomplished by the addition of tetrafluorohydrazine to alkenols or to alkenyl esters followed by hydrolysis. The latter method proved satisfactory in giving the alkanols in good yields and purity. It was demonstrated that the alkanols could be nitrated to yield the difluoramino-containing nitrate esters.

Bis(difluoramines) containing reactive functional groups are of considerable interest and importance in the development of NF chemistry. Petry and Freeman[2] have reported the most comprehensive study of the tetrafluorohydrazine (N_2F_4) olefin addition reaction yielding vicinal bis(difluoramines). Olefins examined were composed of two groups: (a) the simple aliphatic olefins and (b) olefins containing various functional groups such as halo, alkoxy, acetoxy, carbonyl, and aryl. The bis(difluoramines) containing acetoxy, alkoxy, and halo substituents were stable, even when attached to carbon atoms bonded to difluoramino groups, while products containing carbonyl, imino, and hydroxyl groups attached in the α position were prone to decompose with loss of hydrogen fluoride or difluoramine.[3,4] The study of bis(difluoramines) containing various functional groups was expanded to include the preparation of a series of bis(difluoramino)alkanols and their corresponding nitrate esters.

Bis(difluoramino)alkanols.—The preparation of bis(difluoramino)alkanols was accomplished by the direct addition of tetrafluorohydrazine (N_2F_4) to alkenols, or by a more preferred method, the addition of N_2F_4 to a suitable ester derivative of the alkenol followed by hydrolysis or methanolysis to give the alcohol adduct.

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[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021 ORD-11909 (Z).

[2] R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967).

[3] S. F. Reed, *ibid.*, **32**, 2893 (1967).

[4] J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Amer. Chem. Soc.*, **90**, 121 (1968).