

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Free Radical Additions Involving Fluorine Compounds. I. The Addition of Dibromodifluoromethane to Hydrocarbon Olefins

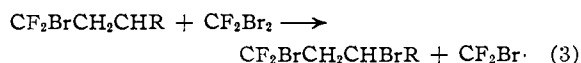
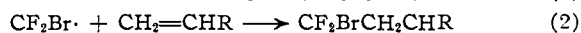
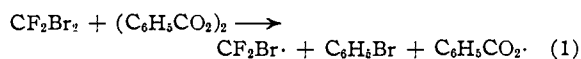
BY PAUL TARRANT AND ALAN M. LOVELACE

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Dibromodifluoromethane has been found to react with hydrocarbon olefins to give 1,3-dibromo-1,1-difluoroalkanes; no reaction occurred with certain chloroolefins. These addition products may be readily converted into 1,1-difluorobutadienes.

The previously reported methods^{1,2} for the preparation of 1,1-difluorobutadienes have been somewhat lengthy and inconvenient and it seemed desirable to find a general method of preparing such compounds by a different procedure. The addition of dibromodifluoromethane seemed to offer an attractive route since it is now commercially available,³ and would give 1,3-dibromides from which it should be possible to remove hydrogen bromide to give 1,3-dienes. Previous work in this Laboratory has shown that neither dichloro-, difluoro- nor trichlorofluoromethane⁴ gives simple addition products with hydrocarbon olefins under conditions in which bromotrichloromethane reacted to give adducts.^{5,6} Some encouragement was offered, however, by the reported reaction of iodotrifluoromethane⁷ with various olefins to give simple products.

It was discovered that dibromodifluoromethane reacted readily with a number of hydrocarbon olefins to give one-to-one addition products in all cases. Undoubtedly the mechanism postulated by Kharasch for the peroxide-catalyzed reaction of bromotrichloromethane to olefins is operative with dibromodifluoromethane



Addition took place readily with propylene, isobutylene, 2-butene and 1-octene and yields of adducts averaging 65–70% were obtained. The reaction with ethylene was sufficiently vigorous to raise the temperature of a 1.4-liter rocking autoclave from 90 to 150° in a very short time; enough pressure was developed to cause breakage of the safety disc which was designed to rupture at 85 atmospheres.

It is of some interest at this point to note that dibromodifluoromethane does not form addition products with chloroolefins under the conditions in which reaction occurs with hydrocarbon olefins. This result is somewhat unexpected in view of the

reactivity of bromotrichloromethane with various chloroolefins.⁶ In most cases with dibromodifluoromethane the unreacted starting materials were almost completely recovered.

Obviously, one of the steps in the reaction is not being completed. It seems likely that step 1 is being carried out since benzoyl peroxide is capable of initiating reaction with hydrocarbon olefins. The trichloromethyl radical must attack the double bond of a chloroolefin and it appears unlikely that the bromodifluoromethyl radical would be any less reactive. If such is the case, then it follows that the chain-breaking step is the last, and results because of the inability of the secondary radical containing chlorine to remove a bromine atom from the CBr_2F_2 .

It was also found in this research that bromotrifluoromethane failed to give any appreciable amount of material boiling higher than the starting material.

The properties of the addition products of dibromodifluoromethane and the various olefins are shown in Table I. It should be noted that no difficulty is involved in the assignment of the structures to the one-to-one addition products with the symmetrical olefins ethylene and 2-butene. In the case of the other compounds, it is possible for addition to take place either to the terminal methylene group or to the adjacent carbon atom. For example, it would thus be possible to obtain either $\text{CF}_2\text{BrCH}_2\text{CHBrCH}_3$ or $\text{CF}_2\text{BrCH}(\text{CH}_3)\text{CH}_2\text{Br}$ from propylene. However, the dehydrobromination of the adduct of propylene and dibromodifluoromethane gave the known² 1,1-difluoro-1,3-butadiene thus proving that the adduct was a straight chain compound. Similarly, the adduct from isobutylene was shown to have the structure indicated in the table by conversion to 1,1-difluoro-3-methyl-1,3-butadiene, the properties of which have been previously reported.¹

Small amounts of materials boiling lower than the addition products were isolated from combined runs from the addition of dibromodifluoromethane to propylene and isobutylene. The physical properties are consistent with compounds having the formulas $\text{C}_4\text{H}_5\text{BrF}_2$ and $\text{C}_5\text{H}_7\text{BrF}_2$, respectively. The butene derivative was oxidized to the known bromodifluoroacetic acid⁸ and thus must be 1-bromo-1,1-difluoro-2-butene. By analogy, the pentene has been assigned the structure $\text{CF}_2\text{BrCH}=\text{C}(\text{CH}_3)_2$; further indirect proof is afforded from the isolation of $\text{CCl}_3\text{CH}=\text{C}(\text{CH}_3)_2$ from the reaction of tetrachloromethane and isobutylene.¹

(8) F. Swarts, *Bull. acad. roy. Belg.*, 597 (1903); *Chem. Zentr.*, 74, II, 709 (1903).

(1) P. Tarrant, J. Attaway and A. M. Lovelace, *THIS JOURNAL*, **76**, 2343 (1954).

(2) P. Tarrant, M. R. Liliquist and J. A. Attaway, *ibid.*, **76**, 944 (1954).

(3) Dow Chemical Company, Midland, Michigan.

(4) A. M. Lovelace, M.S. Thesis, University of Florida, August, 1952.

(5) M. S. Kharasch, O. Reinmuth and W. H. Urry, *THIS JOURNAL*, **69**, 1105 (1947).

(6) M. L. Van Natta, M.S. Thesis, University of Florida, August, 1952.

(7) R. N. Haszeldine, *J. Chem. Soc.*, 1199 (1953).

TABLE I
 THE PROPERTIES OF THE ADDITION PRODUCTS OF OLEFINS AND DIBROMODIFLUOROMETHANE

Olefin	Addition product	Yield, %	B.p. °C.	Mm.	n_D^{20}	d_4^{25}	MRD		Bromine, %	
							Calcd.	Found	Calcd.	Found
$\text{CH}_2=\text{CH}_2$	$\text{CF}_2\text{BrCH}_2\text{CH}_2\text{Br}$		62	86	1.4450	2.0353	31.58	31.16	67.2	66.8
$\text{CH}_2=\text{CHCH}_3$	$\text{CF}_2\text{BrCH}_2\text{CHBrCH}_3$	66.8	60-61	50	1.4469	1.8586	36.20	36.22	63.4	63.7
	$\text{CF}_2\text{BrCH}=\text{CHCH}_3$		76.5	760	1.3872	1.3847	27.97	29.07	39.9	40.4
$\text{CH}_3\text{CH}=\text{CHCH}_3$	$\text{CF}_2\text{BrCH}(\text{CH}_3)\text{CHBrCH}_3$	75	72	39	1.4621	1.7730	40.82	41.22	60.1	59.8
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	$\text{CF}_2\text{BrCH}_2\text{C}(\text{CH}_3)_2\text{BrCH}_3$	64	79	66	1.4632	1.750	40.82	41.48	60.1	60.1
	$\text{CF}_2\text{BrCH}=\text{C}(\text{CH}_3)_2$		96	760	1.4095	1.3476	32.58	33.30	43.2	43.6
$\text{CH}_2=\text{CHC}_6\text{H}_{13}$	$\text{CF}_2\text{BrCH}_2\text{CHBrC}_6\text{H}_{13}$	55	76	1	1.4591	1.4715	59.29	59.57	49.7	50.1

Since the one-to-one saturated products are thermally stable, the olefins must have been formed during the course of the reaction. Such unsaturated compounds are isolated in reactions in which relatively stable methane derivatives such as tetrachloro- or dibromodifluoromethane are used and probably are formed when the radicals, such as $\text{CCl}_3\text{CH}_2\dot{\text{C}}(\text{CH}_3)_2$ and $\text{CF}_2\text{BrCH}_2\dot{\text{C}}(\text{CH}_3)_2$, do not abstract a halogen atom from the methane derivative but instead lose a hydrogen atom.

Alcoholic potassium hydroxide was not suitable for conversion of the 1,3-dibromides into butadienes since high boiling products always were obtained in considerable quantities. However, 1,1-difluorobutadienes were obtained by treating the one-to-one addition products with dimethylaniline or tributylamine at an elevated temperature.

Experimental⁹

1,3-Dibromo-1,1-difluoropropane.—A 1.4-liter stainless steel autoclave was loaded with ethylene (46 g., 1.6 moles), dibromodifluoromethane (1012 g., 4.8 moles) and benzoyl peroxide (15 g., 0.06 mole), sealed and heated to 80° slowly while rocked. At this point an exothermic reaction set in and the rupture disc gave way and most of the contents of the autoclave was lost; however, 176 g. of dark liquid was recovered. Fractionation of this material gave 101 g. of 1,3-dibromo-1,1-difluoropropane with the properties shown in Table I. Undoubtedly yields greater than 23% could be obtained in this reaction. The residue probably contained some two-to-one and higher adducts of the type reported by Joyce, Hanford and Harmon¹⁰ in reactions with ethylene.

1,3-Dibromo-1,1-difluorobutane and 1-Bromo-1,1-difluoro-2-butene.—The stainless steel autoclave was loaded with propylene (34 g., 0.8 mole), dibromodifluoromethane (710 g., 3.3 moles) and benzoyl peroxide (8 g., 0.03 mole). The autoclave was rocked and heated to 85° for four hours. The excess reactants were bled off leaving 182 g. of oil which upon fractionation gave 135 g. of 1,3-dibromo-1,1-difluorobutane, b.p. 60-61° at 50 mm., a yield of 67% based on propylene.

The combined lower boiling material from several runs was refractionated to give a small amount of a compound whose properties, as shown in the table, indicate it to be $\text{C}_4\text{H}_6\text{BrF}_2$. Oxidation of this olefin was accomplished by refluxing for 24 hours in an alkaline potassium permanganate solution. The reaction mixture was acidified with 50% sulfuric acid and filtered. The filtrate was made basic and evaporated to dryness. The white residue was extracted three times with hot 95% alcohol and the extracts evaporated to dryness. The solid was treated with sulfuric acid (96%) and distilled to give material boiling at 155-160°. Swartz reported the boiling point of bromodifluoroacetic acid as 145-160°.

(9) Analyses by: Peninsular ChemResearch, Inc., Gainesville, Florida.

(10) R. M. Joyce, W. E. Hanford and J. Harmon, THIS JOURNAL, 70, 2529 (1948).

1,3-Dibromo-1,1-difluoro-2-methylbutane.—By essentially the procedure described above, 1,3-dibromo-1,1-difluoro-2-methylbutane (586 g., 75% yield) was obtained by heating 2-butene (168 g., 3.0 moles) dibromodifluoromethane (1260 g., 6.0 moles) and benzoyl peroxide (15 g., 0.06 mole) to 100° for four hours.

1,3-Dibromo-1,1-difluoro-3-methylbutane and 1-Bromo-1,1-difluoro-3-methyl-2-butene.—A 65% yield of the saturated one-to-one addition product was obtained by heating for four hours at 80° a mixture of isobutylene (28 g., 0.5 mole), dibromodifluoromethane (512 g., 1.9 moles) and benzoyl peroxide (5 g., 0.02 mole).

The combined lower boiling fractions from a number of runs were redistilled to give a compound which has been assigned the structure $\text{CF}_2\text{BrCH}=\text{C}(\text{CH}_3)_2$ as discussed above.

1,3-Dibromo-1,1-difluorooctane.—A 55% yield of the one-to-one addition product from 1-octene was obtained by heating the olefin (112 g., 1.0 mole), dibromodifluoromethane (878 g., 4.1 moles) and benzoyl peroxide (15 g., 0.06 mole) for four hours at 100°. The physical properties of the adduct are given in Table I.

Addition to 2-Chloropropene.—A 1.4-liter autoclave was charged with 840 g. (4.0 moles) of difluorodibromomethane, 76 g. (1.0 mole) of 2-chloropropene and 10 g. of benzoyl peroxide. The autoclave was rocked and heated for four hours at 100°. The contents of the autoclave were fractionated yielding a total of 909 g. of starting materials. No addition product was obtained.

Addition to 1-Chloropropene.—A 1.4-liter autoclave was charged with 600 g. (2.8 moles) of difluorodibromomethane, 76 g. (1.0 mole) of 1-chloropropene and 10 g. of benzoyl peroxide and treated as above. The contents of the autoclave were fractionated yielding 605 g. of starting materials and 40 g. of dark oil which could not be resolved.

Addition to 2-Chloro-2-butene.—A 1.4-liter autoclave was charged with 840 g. (4.0 moles) of difluorodibromomethane, 97 g. (1.0 mole) of 2-chloro-2-butene and 10 g. of benzoyl peroxide; reaction was carried out as described above for four hours at 100°. Fractionation of the contents of the autoclave yielded 925 g. of starting materials. The small amount of high boiling material yielded no addition product.

1,1-Difluoro-1,3-butadiene.—The adduct from propylene and dibromodifluoromethane (50.4 g., 0.2 mole) was heated to 180° with tri-*n*-butylamine in a flask equipped with a stirrer and reflux condenser connected to traps immersed in Dry Ice. The low boiling material (19 g.) was fractionated to give 9 g. of 1,1-difluoro-1,3-butadiene,² b.p. 3.5-5.0°, for a 50% yield.

1,1-Difluoro-3-methyl-1,3-butadiene.—Using the method described above, the adduct from isobutylene and dibromodifluoromethane (62.5 g., 0.23 mole) and tributylamine (107 g., 0.65 mole) gave a 61% yield (14 g.) of 1,1-difluoro-3-methyl-1,3-butadiene,¹ b.p. 35-36°.

1,1-Difluoro-2-methyl-1,3-butadiene.—A mixture of 1,3-dibromo-1,1-difluoro-2-methylbutane (133 g., 0.5 mole) and tributylamine (343 g., 1.2 moles) was treated as indicated above. Fractionation of the crude product gave 24 g. (23%) of the 1,1-difluoro-2-methyl-1,3-butadiene, b.p. 39°, n_D^{20} 1.3760, d_4^{25} 0.9582; MRD calcd. for $\text{C}_6\text{H}_8\text{F}_2$ 24.35, MRD found 25.18.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{F}_2$: C, 57.6; H, 5.76. Found: C, 57.4; H, 5.47.

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[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

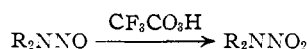
Peroxytrifluoroacetic Acid. I. The Oxidation of Nitrosamines to Nitramines¹

BY WILLIAM D. EMMONS

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A number of secondary nitrosamines have been quantitatively oxidized to the corresponding nitramines with peroxytrifluoroacetic acid, a new reagent.

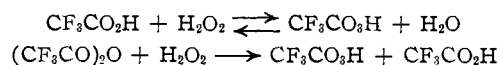
Peroxytrifluoroacetic acid has been found to be a unique reagent for the oxidation of nitrosamines to nitramines and a preliminary report of this work has been published.² Indeed this reagent consti-



tutes in some respects the method of choice for laboratory preparation of very pure secondary nitramines. Previous methods for synthesis of these compounds include the nitrolysis of dialkyl amides³ and Wright's chloride-catalyzed nitration of secondary amines.⁴ The latter method is an excellent one but it is not completely general, and in some cases purification of the products obtained is tedious. In contrast, the oxidation of nitrosamines to nitramines with peroxytrifluoroacetic acid gives a product of high degree of purity in essentially quantitative yield. Since secondary nitrosamines are readily available from nitrosation of the corresponding amines, a new synthesis of nitramines has been established. Previous attempts to oxidize nitrosamines to nitramines have in some cases been partially successful. Thus dinitroxydiethylnitrosamine was converted to dinitroxydiethylnitramine in 32% yield with nitric acid and ammonium persulfate.⁴ The oxidation of nitrosamines to nitramines with hydrogen peroxide and nitric acid also has been reported but this procedure also suffers from the relatively low yield of nitramine obtained.⁵ The superiority of peroxytrifluoroacetic acid over other reagents for nitrosamine oxidation is certainly dependent on the pronounced electrical dissymmetry of the oxygen-oxygen bond caused by the highly electronegative trifluoroacetyl radical. Thus the reagent is even able to oxidize a weakly nucleophilic species such as nitrosamine, probably through transfer of hydroxyl cation, OH⁺, in the transition state.

Peroxytrifluoroacetic acid may be prepared either by addition of 90% hydrogen peroxide to excess trifluoroacetic acid or from trifluoroacetic anhydride and 90% hydrogen peroxide. The latter procedure is to be preferred, however, since with it an anhy-

drous solution containing only peroxytrifluoroacetic acid and trifluoroacetic acid may be obtained in a variety of solvents. Methylene chloride has



proved to be an exceptionally satisfactory solvent for oxidations with peroxytrifluoroacetic acid. It is interesting to note that there is every indication that the equilibrium between peroxytrifluoroacetic acid and water is established very rapidly. Attempts have been made to determine the equilibrium concentration of peroxytrifluoroacetic acid and hydrogen peroxide present in this system. The procedure used for this was that reported by Greenspan and MacKellar which was developed for the concurrent determination of hydrogen peroxide and peracetic acid.⁶ Unfortunately, titration of the hydrogen peroxide in trifluoroacetic acid with ceric ammonium sulfate gave complete recovery of the hydrogen peroxide in every case. Thus it is probable that the equilibrium between hydrogen peroxide and peroxytrifluoroacetic acid is established so rapidly that conventional analytical methods cannot be used to determine equilibrium concentrations.

Some effort has been devoted to a study of the stability of solutions of peroxytrifluoroacetic acid. This work was done primarily to establish the limitations of this reagent as an oxidizing agent so that an intelligent choice of reaction conditions could be made without suffering undue loss of active oxygen by thermal decomposition. Figure 1 represents the results of some of these experiments. Aliquots were removed during each run and the total active oxygen determined by iodometry. It was found that in many cases the decomposition was autocatalytic, and it should be emphasized that the curves are intended only to provide a working knowledge of the stability of peroxytrifluoroacetic acid rather than kinetic data regarding its decomposition. At 25° it was found that a solution of 10 ml. of 90% hydrogen peroxide in 130 ml. of trifluoroacetic acid lost 7% of its active oxygen in 24 hours, 16% in 48 hours and 26% in three days. The most stable solutions were those prepared from trifluoroacetic anhydride and hydrogen peroxide in methylene chloride. Such a solution lost essentially no active

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

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