Patented Oct. 25, 1949 2,486,023

UNITED STATES PATENT OFFICE

2,486,023

NITRO GROUP REPLACEMENT PROCESS

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No Drawing. Application December 21, 1945, Serial No. 636,508

11 Claims. (Cl. 260—652)

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This invention relates to a process for the preparation of aliphatic halohydrocarbons and halocarbons, specifically the alpha-trihalo aliphatic halohydrocarbons and tetrahalomethanes. The invention pertains to the replacement, with halogen, of an —NO_2— group in an alpha-halogenated aliphatic compound.

An object of the present invention is to provide a method whereby alpha-trihalo aliphatic halohydrocarbons and tetrahalomethanes may be prepared. Another object of the invention is the provision of a method whereby alpha-halogenated nitroaliphatic compounds may be treated to produce alpha-trihalo aliphatic halohydrocarbons and tetrahalomethanes. An additional object of the invention is to provide a process for the replacement, with a halogen atom, of an —NO_2— group in an alpha-halogenated aliphatic compound. A preferred object of the invention relates to procedure for the said nitro group replacement with a fluorine atom. A further object of the invention is the provision of a process for the halogenation of alpha-halogenated nitroaliphatic compounds; and a still further object of the invention is the provision of a process for the fluorination of such alpha-halogenated nitroaliphatic compounds. Other objects of the invention will become apparent hereinafter.

In such compounds as trichloromethane, tribromomethane, 1,1,1-trichloroethane, 1,1,1-trichloropropane and other halogenated aliphatic compounds or compounds with halogenated alkyl substituents such as CCl_3—COOH, CCl_2H—COOH, CCl_2H—O—C_2H_5, CCl_3—O—C_2H_5, C_6H_5—O—CH_2—$CHCl_2$, C_6H_5—CCl_3, C_6H_5—CCl_2H, where the halogen atoms, i. e., chlorine and bromine atoms, are situated on the acyclic carbon atoms of the aliphatic compound or substituent it is common knowledge that fluorination first replaces these halogen atoms. It was thus assumed that fluorination of chloropicrin, 1,1-dichloro-1-nitroethane, or 1,1-dichloro-1-nitropropane would also replace the halogen atoms, i. e., chlorine, to yield the corresponding 1-fluoro-1-nitroaliphatic compound. We were surprised that, instead of the expected results, the nitro group was, in every case, preferentially replaced by a fluorine atom. This result heralded an entirely new reaction, the result of which is the exact opposite of the well-known Victor Meyer reaction, which replaces halogen with —NO_2—.

Upon further investigation, we found that chlorination also replaces the nitro group, in this instance, of course, with chlorine. Thus, it is possible, by means of our new process, to prepare

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alpha-trihalo aliphatic compounds by the replacement of the nitrogen in corresponding alpha-halogen-containing nitroaliphatic compounds, such as Cl_3NO_2, CBr_3—NO_2, CH_3—CCl_2NO_2, CH_3—$CHClNO_2$, $CH_3CH_2CCl_2NO_2$, C_2H_5—O—$CH_2CCl_2NO_2$, CCl_2NO_2—COOH, etc. Preferably we use, in this process, lower aliphatic compounds containing not more than eight carbon atoms in the aliphatic chain.

The reaction, in general, comprises subjecting the alpha-halogenated, i. e., alpha-brominated or chlorinated, nitro aliphatic compound, to the action of a halogenating agent, i. e., a fluorinating or chlorinating agent, e. g., hydrogen fluoride, antimony trifluoride, antimony pentafluoride or antimony pentachloride, at a suitable reaction temperature. Usually the reactants were contacted at a low temperature, e. g., zero degrees or Dry-Ice temperature, and then heated to between room temperature and 120 degrees C. for a period varying from four to forty-eight hours. A catalyst may be employed for chlorination, e. g., antimony trifluoride, while antimony V dichlorofluoride may be employed for fluorination. In fluorination, the reaction generated a high pressure, e. g., 250 pounds per square inch, which was usually maintained between 200–220 pounds per square inch by periodically venting the gaseous products. After a sufficient reaction period, the products were removed, washed with dilute alkali, dried and rectified in a five-foot Lecky column. The organic products were then identified by analyses for established physical constants. The products may be separated, purified and used as such, or they may be returned to the reaction for further halogenation.

The apparatus used for the reaction may include a small nickel autoclave or bomb, fitted with reflux condenser, stirrer, safety pressure gauge, and a release valve surmounting the condenser. The release valve allowed products to escape through a collection train comprising a dilute-alkali solution, a drying agent and two traps, the first cooled with ice and the second with a Dry Ice-trichloroethylene mixture. This apparatus proved very satisfactory in conducting the fluorination procedure as herein described. A three-neck, round-bottom flask, fitted with stirrer, reflux condenser and dropping funnel was the reaction vessel for the chlorinations here reported. An electrically heated oil bath was in all cases used to control reaction temperatures.

The fluorination reactions are, during the replacement of the nitro group, catalyzed with a pentavalent antimony salt, either the chloride or

the mixed chloride-fluoride, otherwise thermal decomposition of the organic compound treated usually occurs. The conditions for optimum conversion are indicated in the table following Example 1, and are (*a*) a large excess of hydrogen fluoride, (*b*) presence of a small amount of antimony V dichlorofluoride, (*c*) temperature of about 120 degrees centigrade, and (*d*) pressure of about 220 pounds per square inch. It has also been found that freshly prepared antimony V dichlorofluoride gives higher conversions than the same catalyst after standing for some time in glass. Analogous conditions give optimum yields from the chlorination process.

While the conditions above are optimum for the reactions, we find that temperatures up to 150 degrees centigrade may be employed for both chlorination and fluorination and that pressures from 150 to 300 pounds per square inch allow a good yield from fluorinations.

The following examples illustrate several ways in which the principle of our invention may be applied, but are in no way to be construed as limiting:

Example 1

One mole of chloropicrin (99 milliliters) was reacted with 50 grams of antimony V dichlorofluoride and three moles (60 grams) of hydrogen fluoride in a 900 milliliter nickel bomb equipped with stirrer, reflux condenser, pressure gauge and a release valve atop the reflux condenser. The bomb was heated at 100 degrees centigrade in an oil bath for four hours. In one hour the pressure rose to 200 pounds, where it was maintained for the remainder of the reaction by allowing some of the gases to escape from time to time. After four hours the pressure showed no further rise and heating was discontinued. The gases were then led through a 20 per cent sodium hydroxide solution to remove any hydrogen fluoride and other acidic components, then dried over anhydrous calcium chloride and condensed in two cold traps, the first cooled with ice and the second with a trichloroethylene-Dry Ice mixture. Most of the condensate was caught in the first trap, the second trap condensing mainly decomposition products of chloropicrin identified as phosgene and nitrosyl chloride. Liquid remaining in the reactor was poured into sodium bicarbonate solution and a small amount of chloropicrin recovered therefrom by steam-distillation. The reaction product, colored light yellow due to presence of small amounts of decomposition products, i. e., nitrosyl chloride and phosgene, was rectified in a low-temperature, five-foot Lecky column with liquid take-off, and a 54 gram fraction boiling between 22–22.5 degrees centigrade was collected. This fraction was found to be trichlorofluoromethane, which has an index of refraction at 13 degrees centigrade of 1.3878 using white light. The compound has an observed molecular refraction of 21.8 compared to the calculated value of 21.6. The chlorine:fluorine ratio was also found to correspond to the calculated value, being observed as about 3.

Conversions up to seventy per cent of the theoretical, based on the weight of chloropicrin, may be obtained using optimum reaction conditions as indicated by the following table:

TABLE 1

The fluorination of chloropicrin

Run	Moles of				Time, hrs.,	Temp., ° C.	Press., lbs./ sq. in.	Conversion, per cent
	CCl_3NO_2	SbF_3	HF	$SbCl_2F_3$				
F–1	1	1	3		1	100	0	0
F–2	1		3		20	100	100	0
F–3	1		3		20	100	140	8
F–4	1		3	.20	4	100	200	30
F–5	1		3	3	4	100	100	41
F–6	1	0.33	7.5	.08	3	100	200	60
F–7	1	0.33	7.5	.08	3	120	220	70
F–21 [1]	1		3	.08	3.5	100	150	4
F–22 [1]	0.8		5	.08	4	100	290	20

In runs F–4 to F–7 the pressure was kept constant by venting the apparatus.
[1] The catalyst used here was several months old.

Example 2

One mole of chloropicrin was refluxed with antimony trifluoride and antimony pentachloride in a three-neck, round-bottom flash equipped with stirrer, reflux condenser and dropping funnel. The reaction was heated to 110 degrees centigrade and 80 milliliters of antimony pentachloride was added slowly with vigorous stirring. The temperature, measured at the top of the reflux condenser, was maintained below 85 degrees centigrade, and gaseous products were condensed in a cold trap at —70 degrees centigrade. Considerable nitrosyl chloride and phosgene were removed from the condensate by washing with a 25 per cent solution of sodium hydroxide. Organic products were separated from the aqueous layer, dried over anhydrous sodium carbonate and rectified, yielding 20 grams (13 milliliters) of carbon tetrachloride, boiling about 76–76.5 degrees centigrade, which had been formed by the replacement of $—NO_2—$ with a chlorine atom. The compound formed crystals which melted at —25 degrees centigrade, and had an index of refraction of 1.4637 at 25 degrees centigrade and a molecular refraction of 26.2, in all respects checking carbon tetrachloride. The proposed equation for the reaction is

$$nCCl_3NO_2 + SbCl_5 \rightarrow nCCl_4 + SbCl_5 — n(NO_2)n$$

The solid material remaining in the flask reacted with water to yield a precipitate of antimony oxychloride with evolution of nitrogen tetroxide and was assumed to be antimony nitritochloride.

Example 3

One hundred and sixty-four milliliters of 1,1-dichloro-1-nitroethane was heated to 120 degrees centigrade in a three-neck flask fitted with a dropping funnel, stirrer and reflux condenser, and antimony pentachloride (40 milliliters) was added slowly with rapid stirring. Some decomposition to nitrosyl and acetyl chlorides was evident. The reaction mixture was stirred and heated for one-half hour after the final addition of antimony pentachloride, cooled to room tem-

perature, neutralized with dilute alkali and extracted twice with ether. This ether extract was dried and the ether evaporated on a steam bath. The remaining organic liquid was rectified, found to have a boiling point of 74 degrees centigrade, and identified as methylchloroform.

Example 4

One mole (144 grams) of 1,1-dichloro-1-nitroethane was placed in a nickel autoclave cooled with Dry Ice, and seven and one-half moles (150 grams) of hydrogen fluoride and 20 grams of antimony V dichlorofluoride was added thereto. The autoclave was heated to 115 degrees centigrade and in one-half hour the pressure rose to 250 pounds per square inch. The system was maintained between 200–225 pounds per square inch for four hours by periodic venting of gaseous product, which was passed through a dilute sodium hydroxide solution to remove acidic constituents. The gaseous products were dried over anhydrous calcium chloride and collected in a trap cooled with Dry Ice. Sixty-six grams of crude product was obtained and rectified, yielding 62 grams of an organic compound boiling at —9 degrees centigrade which was identified as 1-chloro-1,1-difluoroethane.

Example 5

One mole (158 grams) of 1,1-dichloro-1-nitropropane was treated with 140 grams of hydrogen fluoride and 20 grams of antimony V dichlorofluoride in a nickel autoclave, cooled with Dry-Ice temperature. The autoclave was heated to 115 degrees centrigrade where a pressure of 250 pounds per square inch was attained in 15 minutes. The pressure was maintained at 220 pounds per square inch by periodic venting of the system over a four-hour period. The gaseous products were passed through dilute sodium hydroxide solution, dried over calcium chloride and collected in a Dry-Ice-cooled trap. Upon rectification of 56 grams of crude product, 50 grams of 1-chloro-1,1-difluoropropane was collected, boiling at 24 degrees centigrade.

Example 6

One-half mole (147 grams) of bromopicrin and six moles (120 grams) of hydrogen fluoride were placed in a small nickel autoclave cooled with Dry Ice. One-half mole of red mercuric oxide was added with stirring. The mixture was allowed to stand at room temperature for 48 hours, during which time the pressure rose to 70 pounds per square inch. The gaseous products were then washed with dilute alkali, dried over anhydrous calcium chloride and collected in a trap cooled with Dry Ice. The organic product, when rectified in a low temperature Lecky column, had a boiling point of —52 degrees centigrade and was identified as bromotrifluoromethane, which boils at —53 degrees centigrade.

While the compounds used in the examples herein are of the straight chain variety, it is to be understood that branched chain nitroaliphatic compounds may also be utilized in the process. For example 1-chloro-1-nitropropane, 1,1-dichloro-1-nitroisopentane, 1,1-dibromo-1-nitroisopentane, 1,1-dichloro-1-nitroisobutane, 1-chloro-1-nitroisobutane, 1,1-dichloro-1-nitroneopentane, 1,1-dichloro-1-nitroisooctane, et cetera, may also be reacted in the process to replace the nitro group situated therein.

We claim:

1. A process for the replacement of a nitro group on a halogenated acyclic carbon atom which includes the step of reacting a lower-aliphatic compound containing in the molecule a primary acyclic carbon atom having attached thereto a nitro group and at least one halogen atom, with a halogenating agent selected from the group consisting of:

(*a*) hydrogen fluoride and a catalyst taken from the group consisting of antimony V chloride, antimony V dichlorofluoride, and mercury II oxide;

(*b*) antimony pentafluoride; and

(*c*) antimony pentachloride,

said reaction being conducted at a temperature below about 150 degrees centigrade, and separating from the reaction product a compound, containing the same number of carbon atoms as the starting compound, wherein the nitro group has been replaced by halogen and the said acyclic carbon atom has attached thereto at least two halogen atoms.

2. The process as claimed in claim 1, wherein the halogenating agent is hydrogen fluoride and antimony V dichlorofluoride at a temperature below 150 degrees centigrade and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one fluorine atom.

3. The process as claimed in claim 1, wherein the halogenating agent is hydrogen fluoride and antimony V dichlorofluoride at a temperature between zero and 120 degrees centigrade and a pressure between 150 and 300 pounds per square inch and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one fluorine atom.

4. The process as claimed in claim 1, wherein the lower-aliphatic compound treated is a 1,1-dihalo-1-nitro compound, wherein the halogenating agent is hydrogen fluoride and antimony V dichlorofluoride catalyst at a temperature between zero and 120 degrees centigrade and a pressure between 150 and 300 pounds per square inch and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one flourine atom.

5. The process as claimed in claim 1, wherein the lower-aliphatic compound is 1,1-dichloro-1-nitroethane, wherein the halogenating agent is hydrogen fluoride and antimony V dichlorofluoride catalyst at a temperature between zero and 120 degrees centigrade and a pressure between 150 and 300 pounds per square inch and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one fluorine atom.

6. The process as claimed in claim 1, wherein the lower-aliphatic compound is 1,1-dichloro-1-nitropropane, wherein the halogenating agent is hydrogen fluoride and antimony V dichlorofluoride catalyst at a temperature between zero and 120 degrees centigrade and a pressure between 150 and 300 pounds per square inch and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one fluorine atom.

7. The process as claimed in claim 1, wherein the halogenating agent is antimony pentachloride and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halo-

gen atoms, including at least one chlorine atom.

8. The process as claimed in claim 1, wherein the halogenating agent is antimony pentachloride and a catalyst comprising antimony trifluoride at a temperature between zero and 150 degrees centigrade and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one chlorine atom.

9. The process as claimed in claim 1, wherein the halogenating agent is antimony pentachloride and a catalyst comprising antimony trifluoride at a temperature between about room temperature and about 120 degrees centigrade and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one chlorine atom.

10. The process as claimed in claim 1, wherein the lower-aliphatic compound treated is a 1,1-dichloro-1-nitro compound, wherein the halogenating agent is antimony pentachloride and a catalyst comprising antimony trifluoride at a temperature between about room temperature

and about 120 degrees centigrade and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one chlorine atom.

11. The process as claimed in claim 1, wherein the lower-aliphatic compound is 1,1-dichloro-1-nitroethane, wherein the halogenating agent is antimony pentachloride and a catalyst comprising antimony trifluoride at a temperature between about room temperature and about 120 degrees centigrade and wherein the compound separated from the reaction product contains an acyclic-carbon-atom having attached thereto at least three halogen atoms, including at least one chlorine atom.

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