water and sodium carbonate was added to bring the solution to *p*H 8 (about 2.2 g. of carbonate was required). The solution was then cooled slightly, and 4.2 g. of KCN was added portionwise, with care, to prevent the temperature of the exothermic reaction from exceeding 90°. After the reaction had subsided, the mixture was warmed on a steam-bath for an hour. The solution containing the salt of cyanoacetate was evaporated to dryness *in vacuo* and to the solid sufficient concentrated HCl was added to bring it to *p*H 1. It was then evaporated to dryness *in vacuo* and the solid was transferred with 30 ml. of concentrated hydrochloric acid into a pressure-stopcock bomb-tube which was placed in boiling water-bath for two hours. After cooling the bomb, the solution was transferred into a distillation apparatus and evaporated to dryness *in vacuo* at 70°. The flask containing the solid residue was placed on a high vacuum line (the flask immersed in a dewar flask containing hot water) and left for six hours on the line which was usually sufficient time to complete drying of the solid. The flask was then removed from the line and the solid was extracted three times with 50 ml. of absolute ether. The ether extracts were pooled and filtered. On evaporating the solvent white crystalline malonic acid separated out; yield 3.8 g. (84% based on chloroacetic acid); melting point 130°; activity 556 μc./mM.

Preparation of $C^{14}H_2(C^{14}N)_2$.—1.00 g. of cyanoacetamide (activity 6.6 μc.mg.), 2.5 g. of phosphorus pentoxide and 0.1 g. lithium chloride were thoroughly mixed. This mixture was heated over an open flame, and the malononitrile thus formed was distilled under vacuum (1 m/m) without delay into a Dry Ice cooled receiver. At the end of the distillation, which should not be allowed to exceed five minutes, the receiver must be returned to room temperature before re-admitting air to preclude the condensation of moisture on the malononitrile; average yield 0.672 g. (85.7%); melting point 32°; activity 8.3 μc./mg. (As determined indirectly from a stable malononitrile derivative.)

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RECEIVED DECEMBER 14, 1950

The Lithium Aluminum Hydride Test for Aromatic Nitro and Nitroso Groups

BY HENRY GILMAN AND THEODORE N. GOREAU

It has previously been reported, in some highly suggestive work, that "the immediate appearance of the azo color upon adding an aromatic nitro compound to lithium aluminum hydride solution at room temperature constitutes a simple and positive test for the nitro group."[1] However, in extending that orienting work it has been found that some aromatic nitro compounds do not give this test when treated in the above manner.

A procedure has been worked out and tested on acids, amides, amines, aldehydes, ketones, phenols, picrates, esters, hydrazines, benzyl halides, salts, ethers and nitriles containing at least one aromatic nitro or nitroso group. In all, sixty-five different compounds were tested, and the presence of the aromatic nitro or nitroso group was detected in each case, except with potassium 2,4-dinitrobenzenesulfonate.[2]

The test was run by making a saturated solution of lithium aluminum hydride in dry ether or ethylene glycol diethyl ether. A saturated solution of the compound to be tested was made using dry ether or dry ethylene glycol diethyl ether as the solvent.[3] The lithium aluminum hydride reagent was added drop by drop to the solution to be tested until an excess of the reagent had been added. The appearance of any definite color or color change in the solution (or in the precipitate, if one is formed) was judged to constitute a positive test. The colors formed were usually various shades of brown, yellow, orange or red.

The color test was confirmed by pouring the reaction mixture into three ml. of water. Aqueous 50% sulfuric acid was added until all of the salts and hydroxides were dissolved, then two ml. of acid was added in excess. A colored solution, other than the color of the original solution of the compound being tested, was taken as confirmatory evidence for a positive test. A definite change of color was shown by comparing the acidified mixture to a blank. The blank was prepared by using the same quantity of test compound and following the same procedure, except that no lithium aluminum hydride reagent was used.

Experimental

4-Nitrophenylacetonitrile.—One ml. of dry ether was saturated with 4-nitrophenylacetonitrile. A saturated solution of lithium aluminum hydride in ether was added drop by drop to the test solution. A bright red color immediately appeared in the solution; it quickly turned very dark, almost black. The reaction mixture was poured into three ml. of water. Aqueous 50% sulfuric acid was added until all of the solid had dissolved, then two ml. of acid was added in excess. The lower, aqueous, layer was colored red.

Lithium 2,4-Dinitrobenzenesulfonate.—One ml. of boiling dry ethylene glycol diethyl ether was saturated with lithium 2,4-dinitrobenzenesulfonate. A saturated solution of lithium aluminum hydride in dry ethylene glycol diethyl ether was added drop by drop until an excess of reagent was added. A very fine precipitate, which gave the solution a muddy appearance, was formed. Fifteen minutes after the addition of the reagent the mixture was poured into three ml. of water. Aqueous 50% sulfuric acid was added until all of the solid had dissolved, then two ml. of acid was added in excess. The lower, aqueous, layer was colored orange-red.

Potassium 2,4-Dinitrobenzenesulfonate.—Since it is known that mixtures of lithium aluminum hydride and certain aromatic nitro compounds darken when exposed to air and that the yields of azo compounds are diminished,[4] a run was made with potassium 2,4-dinitrobenzenesulfonate using increased amounts of reactants in an inert atmosphere. Hydrolysis and acidification subsequent to a two-hour reaction period showed that a definite color change had taken place. When the reaction described above was run without the benefit of an inert atmosphere it was necessary to use a blank in order to confirm the color change.

Approximately 50 mg. of potassium 2,4-dinitrobenzenesulfonate was suspended in 30 ml. of dry ethylene glycol diethyl ether in a dry three-necked flask equipped with a stirrer, a reflux condenser, and a gas inlet tube. The gas inlet tube was connected to a supply of pure, dry nitrogen. The solution was heated to boiling, then the inlet tube was removed momentarily while 10 ml. of a saturated solution of lithium aluminum hydride was rapidly added. After stirring the reaction mixture for two hours a one-ml. aliquot was removed and hydrolyzed with three ml. of water. Aqueous 50% sulfuric acid was added until all of the solid had dissolved, then two ml. of acid was added in excess. The lower, aqueous, layer was dark red-brown.

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(1) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948).

(2) It is thought that the failure of this compound to give a positive test is due to its insolubility, since the free acid and the lithium salt of the acid do give a positive test (see, also, Experimental part).

(3) Ethylene glycol diethyl ether seems to be the better solvent due to the increased solubility of some nitro compounds in this solvent. Lithium aluminum hydride is also more soluble in the glycol ether. The approximate molarities of saturated solutions of our lithium aluminum hydride in diethyl ether and ethylene glycol diethyl ether were found to be 0.83 and 1.1, respectively. Tetrahydrofuran is also a good solvent for this test.

(4) Private communication from Dr. Weldon G. Brown.

Acknowledgment.—The authors thank Donald Esmay, William Meikle and Tse Cheng Wu for confirmatory testing of certain compounds.

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RECEIVED FEBRUARY 3, 1951

The Polymerization of 3,3,3-Trifluoropropene and 2-Methyl-3,3,3-trifluoropropene

BY A. GOLDSCHMIDT

The stabilizing and directing action of the trifluoromethyl group has been plausibly explained by its physicochemical nature, but the failure of α-trifluoromethyl olefins to polymerize, as reported by two sources,[1] has remained obscure. It has been stated that attempts to polymerize 3,3,3-trifluoropropene and 2-methyl-3,3,3-trifluoropropene by free radicals or Friedel–Crafts catalysts were unsuccessful.

Work conducted in these laboratories has shown that these two olefins undergo polymerization in the presence of a free radical forming initiator and of a co-solvent for the monomer and the initiator.[2]

3,3,3-Trifluoropropene could not be polymerized with Friedel–Crafts catalysts under pressures ranging from 90 to 200 p.s.i. and at temperatures of 50–90°. The lack of reactivity of 2-methyl-3,3,3-trifluoropropene in the presence of boron trifluoride contrasts strikingly with the explosive polymerization of its hydrocarbon analog.

It appears that in 1-olefins a trifluoromethyl group adjacent to the double bond promotes the radical-initiated polymerization and inhibits the polymerizing action of Friedel–Crafts reagents.

Experimental

3,3,3-Trifluoropropene, prepared substantially according to the method of Henne and Whaley,[3] and one-tenth its weight of acetyl peroxide (30% solution in dimethyl phthalate) were heated in a chromium–nickel steel reaction vessel for 90 hours at 65°, under a maximum pressure of 250 p.s.i. Upon releasing the pressure, 6% of the monomer was recovered. The dimethyl phthalate was removed by treatment with sodium hydroxide. The polymer is a yellow viscous substance, slightly soluble in hydrocarbons, very soluble in ethyl ether. The elementary analysis showed a fluorine content of 60.1% compared to a theoretical value of 58.2%.

Other initiators successfully used were propionyl peroxide and benzoyl peroxide. Repeated attempts to use the latter without a solvent failed. Dimethyl phthalate, ethyl phenylacetate, 1,4-dioxane and methyl benzoate were found to be suitable co-solvents.

Similarly, $CH_2{=}C(CH_3)CF_3$, prepared from ethyl trifluoroacetate by the method of Swarts,[4] was polymerized in the presence of acetyl peroxide, propionyl peroxide, benzoyl peroxide or *t*-butyl peroxide, with dimethyl phthalate or dioxane as co-solvents. It failed to react in the presence of BF_3 at −80°, 0°, 60° and 100°, even after prolonged contact.

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RECEIVED DECEMBER 16, 1950

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(1) H. B. Hass and M. B. Neher, paper presented at the 109th A. C. S. Meeting in Atlantic City, N. J. (April, 1946); A. L. Henne and S. Kaye, THIS JOURNAL, **72**, 3369 (1950).

(2) British Patent 634,673; U. S. Patent 2,549,580.

(3) A. L. Henne and A. M. Whaley, THIS JOURNAL, **64**, 1157 (1942).

(4) F. Swarts, *Bull. soc. chem. Belg.*, **36**, 191–205 (1927).

A Study of the Peroxide-Catalyzed Chlorination of the Bromotoluenes with Sulfuryl Chloride

BY GORDON L. GOERNER AND RICHARD C. NAMETZ

In this Laboratory Gyorgy[1] has prepared the bromobenzyl chlorides by the chlorination of the three bromotoluenes by the method of Kharasch and Brown.[2] In addition to the desired product there were always obtained low and high boiling fractions which were not identified. Incidental to the preparation of the bromobenzyl chlorides for another problem, we have investigated this chlorination reaction further and have found that the nuclear bromine of these bromotoluenes is replaced by chlorine to a considerable extent and have also found that bromine appears in the side chain. The end products appear to be similar to and in some cases identical with the few compounds which have been isolated from the chlorination of aromatic bromides with gaseous chlorine.[3]

Table I lists the products obtained from the chlorination of the bromotoluenes. In general there were small cuts, probably mixtures, of two to eight grams between the fractions identified. Chlorination of *p*-bromotoluene in the light and in a carbon tetrachloride solvent appeared to increase the yields slightly, that of *p*-chlorotoluene being increased to 28 and 30%, respectively, *p*-bromobenzyl chloride to 47 and 53%, and *p*-bromobenzyl bromide decreased to 11 and 16%, on a distillate basis. In all cases the yield of the chlorobenzyl chlorides was from 1.0 to 2.5%. No chlorobenzyl bromides were found, although their formation in very small yields might be expected. It is interesting to note that the initiation temperature was higher (100° as compared to 93°) when the chlorination of *p*-bromotoluene was performed in the dark. The most satisfactory procedure appears to involve the use of excess bromotoluene as solvent for the reaction.

Kharasch and Brown[2] postulated a free-radical chain mechanism for the chlorination of hydrocarbons with sulfuryl chloride. To the equations which they suggested should be added the following equations for the bromotoluenes, where Cl^-, Br^-, etc., represent free radicals.

$$Cl^- + BrC_6H_4CH_3 \longrightarrow ClC_6H_4CH_3 + Br^- \quad (a)$$
$$Br^- + Br^- \longrightarrow Br_2 \quad (b)$$
$$BrC_6H_4CH_2^- + Br^- \longrightarrow BrC_6H_4CH_2Br \quad (c)$$
$$BrC_6H_4CH_2^- + Br_2 \longrightarrow BrC_6H_4CH_2Br + Br^- \quad (d)$$
$$Br^- + BrC_6H_4CH_3 \longrightarrow BrC_6H_4CH_2^- + HBr \quad (e)$$
$$H^- + Br^- \longrightarrow HBr \quad (f)$$

The products isolated in our investigation may be explained on the basis of (1) the equations of Kharasch and Brown[2] for the introduction of chlorine into the side chain, (2) equation (a) for the introduction of chlorine into the nucleus, and

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(1) H. H. Gyorgy, Ph.D. Thesis, Michigan State College, 1950.

(2) M. S. Kharasch and H. C. Brown, THIS JOURNAL, **61**, 2142 (1939).

(3) F. Asinger, *Monatsh.*, **64**, 153 (1934), summarizes the previous work. Earlier workers isolated only the three bromobenzyl chlorides and *p*-bromobenzyl bromide from the chlorination of the bromotoluenes, although their analytical procedure showed nuclear bromine displacement by chlorine and the appearance of bromine in the side chain.