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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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[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.