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.

TABLE I

PRODUCTS OF THE CHLORINATION OF THE BROMOTOLUENES

Chlorinated	Identified	Yield, %	B.p., Obsd. °C.	Mm.	Lit., °C.	Mm.	n^{20}D Obsd.	Lit.	Characterization
Ortho	*o*-Chlorotoluene	24.5	54–57.5	20	41	11[a]	1.5263	1.5269[a]	Oxid. to *o*-chlorobenzoic acid, m.p. 137–139°
	o-Chlorobenzyl Cl	2.4	97.5–100	17	94	15[b]	1.5621		2-Chloro-5-nitrobenzyl chloride, m.p. 64–66° (rep. 66°[c])
					96–98	14[b]			
	o-Bromobenzyl Cl	32.0	110–114	17	105–106	12[d]	1.5880		
					124–126	20[e]			
	o-Bromobenzyl Br	9.4	124–128	17	129–130	16.5[f]			S-*o*-Bromobenzylisothiourea picrate, m.p. 221.5–223° (rep. 222°[g])
			233–234	743[t]	235–236	743[f,t]			
Meta	*m*-Chlorobenzyl Cl		97–102	17.5	104	17[d]	1.5625	1.5568[h]	Oxid. to *m*-chlorobenzoic acid, m.p. 156–157°
	m-Bromobenzyl Cl		116–118.5	17	119	18[i]			
	m-Bromobenzyl Br[j]		129–133	17	125–127	12[f]			S-*m*-Bromobenzylisothiourea picrate, m.p. 204–205° (rep. 205°[g])
Para	*p*-Chlorotoluene	22 to 30	47.5–50	12	45.5–48	12[k]	1.5209	1.521[k]	Oxid. to *p*-chlorobenzoic acid, m.p. 235–236°
	p-Chlorobenzyl Cl[j]	1.6	94–97	12	94–96	14[l]			*p*-Chlorophenylacetic acid by carbonation of Grignard, m.p. 101.5–103.5°. No dep. with known of m.p. 103–105°
	p-Bromobenzyl Cl[j]	37.6[m] to 53	100–115	12	38–39[n,o]				
			40–41[n]		40[n,p]				
					40–42[n,q]				
	p-Bromobenzyl Br[j]	11 to 18.4[r]	115–124	12	61–62[f,n]				Analysis[s] and mixed m.p.
			60–62[n]						

[a] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 1127. [b] Ref. *a*, p. 867. [c] J. Meisenheimer, *et al.*, *Ann.*, **446**, 225 (1926). [d] G. M. Bennet and B. Jones, *J. Chem. Soc.*, 1818 (1935). [e] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **20**, 665 (1915). [f] Observed on our known preparation. [g] W. J. Levy and N. Campbell, *J. Chem. Soc.*, 1442 (1939). [h] K. Robinson, Ph.D. Thesis, Michigan State College, 1950. [i] S. C. J. Olivier, *Rec. trav. chim.*, 41, 646 (1922). [j] These fractions solidified upon collection. [k] Ref. *a*, p. 1139. [l] Ref. *a*, p. 44. [m] After recrystallization from ethanol the yield was 34.9%. [n] Melting point. [o] G. Errera, *Gazz. chim. ital.*, **18**, 239 (1888). [p] H. Stephan, *et al.*, *J. Chem.*, *Soc.* **117**, 524 (1920). [q] Reference 1. [r] After recrystallization from ethanol the yield was 16.3%. [s] *Anal.* Calcd. for $C_7H_6Br_2$: Br, 63.95. Found: Br, 63.9. [t] Micro b.p.

(3) equations (c), (d) and (e), or some combination of these, for the introduction of bromine into the side chain. Equations (b), (c) and (f) indicate chain terminating reactions. The color changes noted in the reaction mixture as the initiation temperature is approached and the flooding of the condenser with a red liquid at the height of the reaction furnish evidence for equation (b). Since the orange or red color disappears from the reaction mixture very quickly, the free bromine apparently enters into reaction again and may do so according to equation (d).

During the course of this work, the three bromobenzyl bromides were prepared by the bromination of the bromotoluenes at high temperatures in the light. These known bromobenzyl bromides were used for comparison purposes in the identification of the bromobenzyl bromides isolated from the peroxide-catalyzed chlorination reaction.

Experimental

Materials Used.—*o*- and *p*-bromotoluenes were obtained from the Dow Chemical Company and were redistilled before use. The ortho isomer distilled at 75.5° (21.5 mm.) and the para isomer at 82° (27 mm.). *m*-Bromotoluene was obtained from Eastman Kodak Co. and was redistilled.

Sulfuryl chloride, Eastman Kodak Co. practical grade, was distilled immediately before use through a 31-cm. Fenske-type column, b.p. 67° (740 mm.).

Chlorination of the bromotoluenes was carried out in a hood because of the large volume of corrosive gases evolved. In a 3-l. three-necked round-bottomed flask (ground-glass joints) equipped with a thermometer and two bulb condensers and heated by a Glascol mantle were placed 514 g. (3.0 moles) bromotoluene (or an approximately equal volume of bromotoluene and carbon tetrachloride), 135 g. (1.0 mole) of sulfuryl chloride and 0.5 g. (0.002 mole) of benzoyl peroxide. As the reactants were slowly heated to the initiation temperature, the reaction mixture changed from a light yellow to a deep orange color. Near 95° the reaction mixture began to bubble violently, the mantle was instantly removed and the reaction flask chilled in an ice-bath. Even with external cooling the evolution of gases was very vigorous and much red liquid (bromine ?) flooded the condensers. After the reaction ceased (about 20 minutes) the mixture was heated to 110° for a short time.

Chlorination in the dark (with illumination by a selenium ruby red 8 candle power bulb) and in carbon tetrachloride solvent proceeded similarly, except that in the latter case the reaction mixture was still bubbling after five hours.

Distillation of all chlorination products was carried out through a Fenske-type column, 31 cm. in length, packed with $^1/_{16}$ in. glass helices with a take-off of the cold finger type. All corrosive gases were removed by a water aspirator and the remaining liquid fractionated at the reduced pressure of an oil pump. Cuts of 1 to 3 ml. were usually taken.

The bromobenzyl bromides were prepared by a modification of the procedure of Coleman and Honeywell[4] for the preparation of *p*-nitrobenzyl bromide. The bromine (1.0 mole) was added with stirring beneath the surface of an excess of bromotoluene (2.0 moles) at such a rate that the solution was kept just free of bromine color. The reaction mixture was illuminated by two 150-watt, unfrosted tungsten lamps. During the addition of the bromine, the temperature of the reaction mixture, 100° at the start, rose rapidly to 135–140° for the ortho, 175–180° for the meta, and 110–120° for the para isomer. Distillation through the Fenske-type column gave *o*-bromobenzyl bromide, b.p. 129–130° (16.5 mm.), in 79.2% yield. *m*-Bromobenzyl bromide, b.p. 125–127° (12 mm.), 74% yield, solidified as collected (reported m.p., 40°[5]). *p*-Bromobenzyl bromide, b.p. 125–135° (12 mm.), was obtained in 52% yield after recrystallization from ethyl alcohol, m.p. 61–62.5° (reported 63°[5]).

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RECEIVED DECEMBER 15, 1950

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[4] G. H. Coleman and G. E. Honeywell in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 443.

[5] J. B. Shoesmith and R. H. Slater, *J. Chem. Soc.*, 219 (1926).