method is described by E. S. Johnson[4] and Harding and Doran.[5] The activities of the precipitates were measured, no account being taken of differences in self absorption or back scattering. Multiplying the total measured activity for a run by the ratio of the equivalents of sulfur in the carbon disulfide to the total equivalents gave the expected activity. The ratio of the activity observed in the copper xanthate to that expected gave the "% exchange."

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[4] E. S. Johnson, This Journal, **28**, 1209 (1906).

[5] Harding and Doran, *ibid.*, **29**, 1476 (1907).

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The Exchange between Br_2^* and $HgBr_2$ in Carbon Disulfide Solution

BY DAVID L. DOUGLAS, ROBERT A. COOLEY AND DON M. YOST

The exchange of bromine atoms between bromine and various inorganic bromides has been previously reported.[1-3] In view of the lack of published quantitative data and because of the general usefulness of the reaction in preparing samples of pure radioactive bromine, we are reporting some work done in this Laboratory in 1941. A study was made of the exchange of Br^{82} atoms between Br_2^* and $HgBr_2$ in carbon disulfide solution. The results of six experiments showed that the exchange is complete within at least two and one-half minutes at somewhat less than 0°. Table I contains the details of the experiments and results.

TABLE I

EXCHANGE OF BROMINE BETWEEN MERCURIC BROMIDE AND BROMINE IN CARBON DISULFIDE AT 0°[4]

Reaction time, sec.	Concentrations in moles/liter × 10^3		Measured activity (cor.)		Fraction of Br_2 actually measured	Exchange, %
	Br_2	$HgBr_2$	Br_2	$HgBr_2$		
245	6.82	1.67	1136 ± 10	274 ± 2	1.00	99 ± 2
266	6.82	1.67	992 ± 8	362 ± 3	0.854	121 ± 2
324	1.34	1.67	82 ± 1	252 ± 6	.406	100 ± 3
290	1.34	1.67	130 ± 1	250 ± 5	.650	100 ± 3
245	6.26	1.67	3066 ± 18	1160 ± 7	.666	96 ± 1
157	6.26	1.67	2863 ± 16	1318 ± 9	.593	102 ± 1

Experimental.—Radioactive bromine was prepared in the usual manner by irradiating *n*-butyl bromide with neutrons from a Rn–Be source. A solution of the active bromine in reagent carbon disulfide was prepared and analyzed by standard methods. The mercuric bromide solution was prepared by weighing out the pure solid into a known volume of carbon disulfide.

The actual exchange reaction and separation were carried out as follows: 5 ml. of the solutions of Br_2^* and $HgBr_2$, cooled to 0°, were pipetted into a 250-ml. distilling flask which was surrounded by an ice-bath. As soon as the solutions were mixed thoroughly the bromine and carbon disulfide were distilled off in a vacuum and collected in a trap at −78°. The time elapsed from the moment of mixing to the completion of the distillation is recorded in column 1 of Table I. Clearly the temperature dropped below 0° during this time; however, no attempt was made to measure this drop.

The bromine was reduced and precipitated as silver bromide. The mercuric bromide residue in the flask was dissolved in nitric acid and the bromine precipitated as silver bromide. The activities of the precipitates were measured by counting techniques. Determination of the fraction of the bromine which was actually trapped was accomplished by analyzing the silver bromide precipitate.

The activities were corrected for time of measurement and background—the short lived activity being allowed to decrease to a negligible value before use. The "% exchange" was calculated thus

$$\% \text{ exchange} = \frac{\text{Activity from } HgBr_2}{\text{Fraction of } Br_2 \text{ measured}} \times \frac{100}{\text{Mole fraction } Br_2 \text{ in } HgBr_2\text{–}Br_2 \times \text{Sum of activities}}$$

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[1] J. N. Wilson and R. G. Dickinson, This Journal, **61**, 3519 (1939).

[2] Kolthoff and O'Brien, *J. Chem. Phys.*, **7**, 401 (1939).

[3] R. Muxart, *Compt. rend.*, **224**, 1107 (1947).

[4] R. A. Cooley, Ph.D. Thesis, Cal. Tech., 1941.

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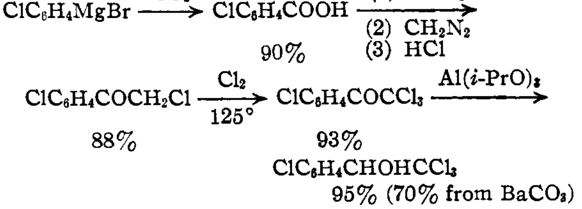
p-Chloro-α-(trichloromethyl)-benzyl Alcohol and a Chlorination Apparatus

BY EDWARD M. FRY

At the time the insecticidal value of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane became evident very little was known of its toxicology and as part of a program aimed at evaluating these properties a synthesis designed to utilize isotopic carbon at the point of attachment of the two chlorophenyl rings was undertaken. However, rapid and widespread use of DDT soon revealed its low toxicity with respect to humans and the project was discontinued, the synthesis being halted at *p*-chloro-α-(trichloromethyl)-benzyl alcohol. Carbon dioxide containing isotopic carbon was not used in this investigation and as none of the intermediate compounds are new, nor were any new or improved synthetic procedures used, the work is of interest only with respect to the method used with brief mention of experimental conditions. The scheme is as follows



$$ClC_6H_4MgBr \xrightarrow{CO_2} \underset{90\%}{ClC_6H_4COOH} \xrightarrow[\substack{(2)\ CH_2N_2 \\ (3)\ HCl}]{(1)\ SOCl_2}$$

$$\underset{88\%}{ClC_6H_4COCH_2Cl} \xrightarrow[125°]{Cl_2} \underset{93\%}{ClC_6H_4COCCl_3} \xrightarrow{Al(i\text{-}PrO)_3}$$

$$\underset{95\%\ (70\% \text{ from } BaCO_3)}{ClC_6H_4CHOHCCl_3}$$

Carbon dioxide generated from barium carbonate reacted in a threefold excess of 1 *N* Grignard reagent to give the acid. The acid chloride in benzene solution reacted with cold ethereal diazomethane, then in the cold with dry hydrogen chloride to give *p*,α-dichloroacetophenone. The ketone in an equal volume of trichloroacetic acid on treatment with chlorine for two days at 120–125° gave *p*,α,α,α-tetrachloroacetophenone which, on reduction with a small excess of 3 *N* aluminum isopropoxide in isopropyl alcohol, gave the alcohol.