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."

(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 × 10^4 Br_2	$HgBr_2$	Measured activity (cor.) Br_2	$HgBr_2$	Fraction of Br_2 actually measured	Exchange, %
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

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

(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

$$ClC_6H_4MgBr \xrightarrow{CO_2} ClC_6H_4COOH \xrightarrow[(2)\ CH_2N_2\ (3)\ HCl]{(1)\ SOCl_2} ClC_6H_4COCH_2Cl$$

90%

$$ClC_6H_4COCH_2Cl \xrightarrow[125°]{Cl_2} ClC_6H_4COCCl_3 \xrightarrow{Al(i\text{-}PrO)_3} ClC_6H_4CHOHCCl_3$$

88% 93% 95% (70% from $BaCO_3$)

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.

Chlorobenzoic acid has been prepared in the above manner,[1] and also from the corresponding lithium compound.[2] *p*,α-Dichloroacetophenone has been made by the action of chlorine on *p*-chloroacetophenone,[3] and by the action of chloroacetyl chloride on chlorobenzene.[4] *p*,α,α,α-Tetrachloroacetophenone has been made by the action of chlorine on *p*,α,α-trichloroacetophenone,[3] and *p*-chloro-α-(trichloromethyl)-benzyl alcohol by the condensation of chloroform with *p*-chlorobenzaldehyde.[5] This alcohol was also found to be a constituent of technical DDT.[6]

The apparatus described below was constructed so that the effect of solvent, temperature and light on chlorine reactions could be followed manometrically. Circulation of the gas is required for the removal of hydrogen chloride, and the corrosive action of moist chlorine makes a glass apparatus necessary. Circulation is achieved by means of an aspirator actuated by a stream of carbon tetrachloride–water which also serves to remove hydrogen chloride. The diagram shows the aspirator unit on the left, the reaction flask with a small condenser in the center, and the chlorine reservoir on the right. Movement of chlorine is in a clockwise direction and its absorption is followed by means of a manometer shown at the center hole of the reservoir stopper. The device proved a valuable index to the rate of chlorination under varying conditions and gave an estimate of the amount reacted. Sources of error are diluents such as air and gaseous decomposition products.

Construction and Operation.—Although a single five-gallon bottle is shown as the reservoir, more than one connected in series may be more convenient. The rubber stopper was substantially unaffected after several months in contact with chlorine. Chlorine is appreciably soluble in the carbon tetrachloride–water mixture used in the aspirator unit, and when the aspirator is shut off its pressure must be high enough so that its subsequent absorption by the cooling carbon tetrachloride–water does not result in manometer water being sucked into the reservoir. The manometer is long enough to measure a pressure of about 80 cm. of water. Chlorine should be added only when the aspirator flask is hot. Otherwise expulsion of chlorine from the hot carbon tetrachloride–water might cause such an increase in pressure as to blow the water from the manometer and release chlorine into the room. A drop in atmospheric pressure or a rise in room temperature can have the same effect if the apparatus is operated too closely to the pressure limit of the manometer. Changes of this nature during a run are observed and corrected for by means of a blank manometer (not shown). If dry chlorine is desired, calcium chloride is used to fill the enlarged portion of tubing extending to the bottom of the bottle.

To fill the apparatus, flask A, equipped with an electric heating jacket and containing carbon tetrachloride and water, is heated until its contents begin to boil. Chlorine is then slowly admitted through stopcock E, stopcock D being turned so as to deflect the chlorine into the reservoir and allow the displaced air to escape into the hood. The displacement of air is followed visually and when completed stopcock D is turned to the illustrated position and the pressure in the system brought to the desired level. Stopcocks B and C are for the purpose of isolating the reaction flask so that it can be removed with negligible chlorine loss.

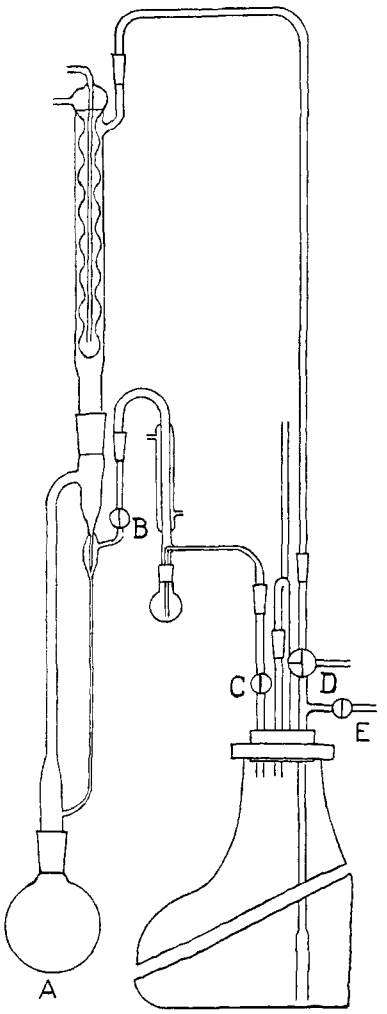

Fig. 1.

The various parts of the apparatus are connected with 24/40, 10/30, and 14/20 joints, lubricated with Dow-Corning silicone grease, and in the two smaller sizes held together with rubber bands secured between hooks (not shown). It is felt that ball-type joints would be more satisfactory than the 10/30 joints in that the apparatus could be allowed to stand unused for longer periods of time without danger of freezing at these relatively fragile junctures. The lubricant is slowly hardened by chlorine. The only construction feature requiring care is that of the aspirator unit. The tube should be symmetrically placed in the throat taper and about 1 mm. in diameter at the tip. Four mm. O. D. tubing was used for both the inner aspirator tube and for the discharge column which was found to operate best at a length of 20 cm., the range for satisfactory operation being between 15 and 25 cm. A rate of from 60–80 bubbles a minute against a head of 5 cm. of water was realized and the efficiency of the aspirator appears to be greatest with a moderate rate of reflux.

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(1) Bodroux, *Compt. rend.*, **137**, 711 (1903).
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(3) Gautier, *Ann. chim. phys.*, [6] **14**, 387–404 (1888).
(4) Collet, *Compt. rend.*, **125**, 718 (1897).
(5) Howard, THIS JOURNAL, **57**, 2317 (1935).
(6) Haller, *et al.*, *ibid.*, 1591 (1945).