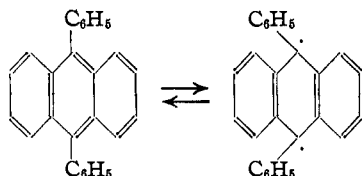


but on the basis of the structure of anthracene (particularly its *meso*-diaryl derivatives). Dufraisse⁴ has recently suggested that the reactivity of these compounds, especially their ability to form peroxides on exposure to oxygen, is analogous to the behavior of triarylmethyl radicals, and that these molecules actually exist to some extent as di-radicals.



Experimental

Reagents.—Anthrone, prepared from anthraquinone,⁵ was reduced to anthracene according to Martin's directions.⁶ The anthracene crystallized as plates which melted at 216–216.5° (corr.) and which showed a deep purple fluorescence. Commercial dioxane was purified according to the directions of Scatchard and Benedict,⁷ b. p. 100.5–101° (corr.). Bromine was purified as before.¹ The purified dioxane did not react with this bromine, even up to 75°.

Procedure.—Standard bromine and anthracene solutions (ca. 1%) in dry dioxane (protected from atmospheric moisture) were mixed. Canary yellow needles separated in one minute. At the end of fifteen minutes the reaction mixture was poured into water containing potassium iodide. The bromine consumed by one sample was 0.0496 mole and

(4) Dufraisse, *Bull. soc. chim.*, [5] 6, 422 (1939).

(5) "Organic Syntheses," Coll. Vol. I. John Wiley and Sons, Inc., New York, N. Y., 1931, p. 52.

(6) Martin, *THIS JOURNAL*, 58, 1438 (1936).

(7) Scatchard and Benedict, *ibid.*, 58, 837 (1936).

the hydrogen bromide evolved 0.0494 mole, by another 0.0472 and 0.0463 mole, respectively, the required values for the equation of the formation of 9,10-dibromoanthracene. This substance was isolated by filtration after the titrations. It formed canary yellow needles from acetic acid, m. p. 221° (corr.). From a 0.50-g. sample, 0.93 g. (99%) was obtained.

If precautions to exclude atmospheric moisture were not observed, 9-bromoanthrone and anthraquinone were isolated as well. In a particular experiment, 5 cc. of water and 1.2 g. each of bromine and anthracene were added to 95 cc. of dioxane. A sample of this mixture showed a ratio of 0.0566 mole of bromine consumed to 0.0996 mole of hydrogen bromide evolved. After thirty minutes the reaction mixture was poured into 100 cc. of water. The precipitate (0.6 g.) was recrystallized from benzene-petroleum ether to give thick square plates of 9-bromoanthrone (I), m. p. 142–144° (corr.), with decomposition.⁸

Anal. Calcd. for C₁₄H₉OBr: Br, 29.30. Found: Br, 29.35.

Extraction of the aqueous filtrate with ether, followed by evaporation of the solvent, yielded 0.6 g. of pale yellow needles of anthraquinone, m. p. 280–282° (corr.).

When a higher percentage of water was added, all the bromine consumed appeared as hydrogen bromide and the sole product was anthraquinone.

Summary

Unless moisture is excluded rigorously, the reaction of bromine with anthracene in dioxane leads to the formation of 9-bromoanthrone and anthraquinone, as well as the normal product, 9,10-dibromoanthracene.

(8) Goldman (*Ber.*, 20, 2437 (1887)) and Meyer (*Ann.*, 379, 62 (1911)) each report a melting point of 148°.

URBANA, ILLINOIS

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

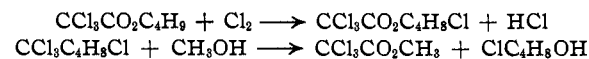
Chlorination of Butyl Trichloroacetates

BY HOWARD M. WADDLE AND HOMER ADKINS

The direct chlorination of *n*-butyl, *i*-butyl and *s*-butyl trichloroacetates seemed to offer a method for the preparation of chlorobutanols and of ascertaining the relative reactivity toward chlorine of hydrogens on primary, secondary and tertiary carbon atoms.¹

Buffet found that *n*-butyl trichloroacetate could be rather rapidly chlorinated at 110–120° under the light from a 150-watt tungsten electric light bulb. Various monochlorobutyl trichloroacetates were formed which could be methanolized to the corresponding chlorobutanols.

(1) Geo. M. Buffet, Ph.D. Thesis, University of Wisconsin, Madison, 1933.



Later experience showed that it was preferable to separate carefully the chloro-esters by fractional distillation and to saponify the pure esters, rather than to attempt to separate the alcohols obtained by methanolysis or hydrolysis of a mixture of esters.

n-Butyl, *i*-butyl and *s*-butyl trichloroacetates were prepared in 82 to 89% yields by refluxing two moles of trichloroacetic acid and four moles of the alcohol for six to eight hours. The excess alcohol and water were removed by distillation through a Vigreux column, 35 cm. in length. Emulsions are likely to be formed if the alcohol is not rather completely removed before the crude esters are

washed with 10% sodium carbonate solution. The esters were then washed with water, dried over calcium chloride and distilled under reduced pressure at temperatures no higher than 100°. An automatic separator proved useful in the preparation of *s*-butyl trichloroacetate.

The chlorinations were carried out in a liter, round-bottomed, Pyrex flask provided with three side arms. A stirring device, operating through a mercury seal, was placed in the neck of the flask. A thermometer well, an inlet tube for chlorine and a water-cooled reflux condenser were connected through the side arms of the flask. The chlorine passed through a wash bottle² containing sulfuric acid into a liter flask and then through a flowmeter and capillary tube into the bottom of the reaction mixture. The exit gases from the reaction mixtures passed up through a coil condenser.

The procedure for chlorination was as follows. Two moles of the ester (440 g.) was placed in the reaction flask and heated to 120° in an electrically heated and controlled oil-bath.³ A 200-watt clear glass, tungsten light bulb was placed 5 cm. from the surface of the reaction flask which was immersed in the oil-bath to the top of the liquid in the flask. Chlorine was then passed in at the rate of 15 to 20 g. per hour, the reaction mixture being kept at 120 ± 2°. Chlorination was continued (seven to ten hours) until the increase in weight of the reaction flask corresponded to two moles of chlorine (69.9 g.). The product was water white.

The reaction mixtures after chlorination were separated into their components by the use of a packed column of the total reflux-partial take off variety. The packed section of the column was 18 mm. in diameter and 100 cm. in length surrounded by an evacuated jacket. The packing consisted of helices containing 1 to 2 turns, 7 mm. in diameter and made from glass rod 1 mm. in diameter. The air space about the evacuated jacket was electrically heated and maintained at a constant temperature by controlling the current passing through a heating unit of nichrome wire. The pressure within the column during fractionation was held constant by means of a manostat.⁴

The esters were distilled from a flask, immersed in an electrically heated and controlled oil-bath, and connected to the column by a ground glass joint. The procedure used in operating the column is well outlined by Morton.⁵ The first distillation of a reaction mixture (510 g.) was carried out rather rapidly during thirty-six hours divided into three intervals. The second fractionation required sixty hours divided into 6 intervals, the reflux ratio being about 20 to 1. Ebullition tubes were not used.

Each of the three butyl trichloroacetates gave four fractions: A, unchanged ester, B and C, two different monochlorobutyl trichloroacetates, and D, a dichlorobutyl trichloroacetate. The weights of the fractions from chlorinated *n*-butyl trichloroacetate (510 g.) were A, 78 g., B, 158 to 175 g., C 93 g. and D, 50 g. From the chlorinated *i*-butyl ester (510 g.) the corresponding weights were A, 81 g., B, 118 to 122 g., C, 139 g. and D, 41 to 56 g., while from

the chlorinated *s*-butyl ester (508 g.) the weights were for A, 83 to 84 g., B, 137 to 144 g., C, 122 to 130 g. and D, 21 to 37 g.

The fractions containing the mono- and dichlorobutyl trichloroacetates were washed with 2% sodium carbonate solution and with water, dried over calcium chloride and refractionated. The monochloro esters were rather rapidly distilled, with ebullition tubes, through a Vigreux column 7 cm. in length, while for the dichloro esters a modified Widmer with a spiral 12 cm. in length was used. Data on the physical properties of the various esters are given in Table I.

The ester was saponified at temperatures below 35° during the course of five to seven hours. The ester was rapidly stirred while an equivalent molecular amount of sodium hydroxide in a 10% solution in water was added over a period of several hours. After saponification was complete the solution was extracted continuously with ether for twelve hours. After removal of the ether the chloro-alcohol was distilled under reduced pressure through a modified Widmer column having a spiral 20 cm. in length. A capillary ebullition tube for the inlet of air was used in the distillation.

Chlorobutanols were obtained from five of the nine chloro esters which were isolated. Certain physical properties and the analyses of the alcohols, and the melting point and analyses of their phenyl urethans are given in Table I.

The lower boiling monochloro esters (the fractions labeled B) from the *i*-butyl and *s*-butyl esters reacted with sodium hydroxide much more slowly than in the case of the five esters referred to just above. Approximately one-half of the ester was recovered unchanged after reaction for several hours with a molecular equivalent of sodium hydroxide. *i*-Butyraldehyde was detected among the products from the saponification of the monochloro-*i*-butyl ester. The saponification of this latter ester (32 g.) was then attempted, using two molecular equivalents of sodium hydroxide at 75° for three hours. A stream of nitrogen was passed through the reaction mixture to remove *i*-butyraldehyde as rapidly as it was produced. The aldehyde (5 g.) was condensed in a trap surrounded with solid carbon dioxide. It was identified by boiling point and the formation of a 2,4-dinitrophenylhydrazone, m. p. 185°. There was also obtained 4 g. of a compound, b. p. 69–70° (7 mm.), which was halogen-free and appeared to be a glycol. It was not identified.

The saponification of the lower boiling monochloroester from *s*-butyl trichloroacetate gave no products boiling above 56° and only a small amount of that compound. No other liquid product was obtained by saponification with two moles of sodium hydroxide at 40°. Sufficient quantities of the fractions containing the dichloro esters from *i*-butyl and *s*-butyl trichloroacetates were not available for saponification studies.

The data given above may be summarized as follows. There remains after the reaction of one mole of chlorine with one mole of *n*-, *i*- or *s*-butyl trichloroacetate at 120° approximately 0.2 mole of unchanged ester, a little over 0.5 mole of monochloroesters and a few hundredths of a mole of

(2) McKenney, *Ind. Eng. Chem., Anal. Ed.*, **6**, 258 (1934).

(3) Waddle and Imhoff, *J. Chem. Ed.*, **15**, 191–192 (1938).

(4) Hershberg and Huntress, *Ind. Eng. Chem., Anal. Ed.*, **5**, 144 (1933).

(5) Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., p. 83.

TABLE I
 PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	B. p.		n_D^{25}	d_4^{25}	M_D		Chlorine, %	
	°C.	Mm.			Calcd.	Found	Calcd.	Found
<i>n</i> -Butyl alcohol ^a	100-101	24	1.4495	1.266				
<i>i</i> -Butyl alcohol ^a	93-94	24	1.4456	1.255				
<i>s</i> -Butyl alcohol ^a	88-89	19	1.4440	1.252				
2-Chlorobutanol-1 ^a	94-96	5	1.4728	1.390	51.03	51.24	55.8	55.3
4-Chlorobutanol-1 ^a	113-116	5	1.4800	1.417	51.03	50.92	55.8	56.0
Dichlorobutanol-1 ^a	127-131	5	1.4930	1.497	55.98	55.89	61.5	60.7
2-Chloro-2-Me-propanol-1 ^a	80-81	5	1.4658	1.369	51.03	51.35	55.8	55.6
3-Chloro-2-Me-propanol-1 ^a	98-99	5	1.4742	1.397	51.03	51.22	55.8	55.7
Dichloro-2-Me-propanol-1	101-105	5	1.4862	1.477	55.98	56.04	61.5	60.2
3-Chlorobutanol-2 ^a	83-84	5	1.4671	1.373	51.03	51.34	55.8	55.8
1(?) -Chlorobutanol-2 ^a	91-93	5	1.4713	1.395	51.03	50.89	55.8	55.8
Dichlorobutanol-2 ^a	108-110	5	1.4850	1.475	55.98	55.06	61.5	61.7
2-Chlorobutanol-1	74-76	25	1.4410	1.062	27.06	26.99	32.7	33.3
4-Chlorobutanol-1	72-75	10	1.4551	1.125	27.06	26.18	32.7	36.0
Dichlorobutanol-1	87-93	6	1.4786	1.273	31.93	31.73	49.6	50.3
3-Chloro-2-Me-propanol-1	76-78	21	1.4460	1.083	27.06	26.74	32.7	33.2
1(?) -Chlorobutanol-2	56	12						
	68-70	27	1.4410	1.068	27.06	26.86	32.7	32.6
	M. p.				Carbon, %		Hydrogen, %	
2-Chlorobutanol-1 ^b	52.5-53.5				58.02	58.10	6.20	6.37
4-Chlorobutanol-1 ^b	54-55				58.02	58.16	6.20	6.44
3-Chloro-2-Me-propanol-1 ^b	63.5-64				58.02	58.07	6.20	6.52
1(?) -Chlorobutanol-2 ^b	78.5-79				58.02	58.03	6.20	6.42

^a Trichloroacetate. ^b Phenyl urethan.

dichloroesters. About 25% of the original ester has not been accounted for except in intermediate fractions and the residue after distillation.

From each of the three butyl trichloroacetates two different monochlorobutyl esters have been produced and separated by fractionation. The structures tentatively assigned to these six alcohols, separated as trichloroacetates, are given below. The figures given after each formula represent the moles of ester isolated from the reaction of one mole of a butyl ester and one mole of chlorine.

I	$\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{OH}$	0.33
II	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.19
III	$(\text{CH}_3)_2\text{CClCH}_2\text{OH}$.24
IV	$\text{ClCH}_2\text{CHCH}_2\text{OH}$.27
	 CH_3	
V	$\text{CH}_3\text{CHClCHOHCH}_3$.28
VI	$\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{Cl}$	
	or $\text{ClCH}_2\text{CH}_2\text{CHOHCH}_3$.25

Four of the alcohols, I, II, IV and VI, have been obtained in a pure state in yields of 83, 86, 76 and 44%, respectively, from the saponification of the esters. The esters of the other two alcohols, III and V, underwent other reactions as well as saponification when attempts were made to prepare the alcohols.

The evidence for the structures suggested for the alcohols is as follows. The chlorobutanol believed to have the structure I was converted into the dichloride through the use of thionyl chloride and pyridine.⁶ The dichlorobutane so obtained has a b. p. of 127°, n_D^{25} 1.4420, n_D^{15} 1.4468, which agrees with the values of b. p. 124° and n_D^{15} 1.4474 reported by Navez.⁷ The 1,3-dichlorobutane is reported to boil somewhat higher.⁸ It is quite possible that both the 2- and 3-chlorobutyl esters were produced by chlorination.

4-Chlorobutanol-1 was prepared from tetrahydrofuran⁹ and its phenyl urethan compared with the phenyl urethan of the alcohol, II, believed to have that structure. The boiling points and refractive indices of the two samples of the alcohol and the melting points and mixed melting points of the phenyl urethans, 54-55°, showed them to be identical.

Formulas III and IV represent the only possible chloro-*i*-butanols. An ester of the alcohol IV would boil higher than an ester of the alcohol III, so that formula III is assigned to the alcohol

(6) Clark and Streight, *Proc. Roy. Soc. Canada*, **23**, 111, 77 (1929).

(7) Navez, *Bull. soc. chim. Belg.*, **39**, 435 (1930).

(8) Fargher and Perkin, *J. Chem. Soc.*, **105**, 1356 (1914).

(9) Starr and Hixon, *THIS JOURNAL*, **56**, 1595 (1934).

of the lower boiling ester. The attempted saponification of this lower boiling ester gave *i*-butyr-aldehyde as the only definitely characterized product. The rearrangement of a chloro alcohol of the type of III to an aldehyde is an orthodox reaction.

All three of the possible chloro-*s*-butyl alcohols have been reported, but solid derivatives have not been prepared nor the physical properties of the alcohols carefully defined. 3-Chlorobutanol-2, b. p. 138–139° (753 mm.), was prepared by the addition of hypochlorous acid to butene-2.¹⁰ 4-Chlorobutanol-2, b. p. 70° (13 mm.), has been prepared from methylmagnesium iodide and β -chloropropionaldehyde.¹¹ 1-Chlorobutanol-2, b. p. 52° (15 mm.), has been prepared by the reaction of chloroacetaldehyde and ethylmagnesium bromide.¹²

The 3-chloro alcohol would be the lowest boiling of the isomers, and would be the more unstable. It therefore seems probable that the lower boiling of the monochloro esters derived from *s*-butyl ester would be an ester of the 3-chloro isomer. All attempts to saponify this ester gave products such

(10) Henry, *Compt. rend.*, **145**, 499 (1907).

(11) Krassuski, *ibid.*, **145**, 763 (1905).

(12) Fourneau and Ramart-Lucas, *Bull. soc. chim.*, [4] **25**, 367 (1919).

as would correspond to *sym*-dimethylethylene oxide. This is a not unexpected result for the ester of such an alcohol. It should be noted that the ester of similar structure from *i*-butyl trichloroacetate also failed to give a chloro alcohol upon saponification.

There is no adequate basis for deciding whether the chlorobutanol-2 isolated was the 1- or 4-chloro compound. The boiling point is close to that reported for the 1-chloro compound. It would appear that the 4-chloro compound boils somewhat higher.¹⁰ The low yield of alcohol obtained by saponification also suggests the 1-chloro isomer since the 4-chloro alcohol would have a structure similar to 3-chloro-2-methylpropanol-1, which was obtained in excellent yield from its trichloroacetate.

Summary

The *n*-, *i*- and *s*-butyl trichloroacetates have been chlorinated and in each case two monochlorobutyl trichloroacetates have been separated as the major products of chlorination. The corresponding monochlorobutyl alcohols have been obtained in four cases by saponification of the esters while in two cases attempts at saponification failed to yield the alcohols.

MADISON, WISCONSIN

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Relative Oxidation Potentials of Ketones

BY FRED W. COX¹ AND HOMER ADKINS

Ketones may be arranged in a series according to their strength as oxidizing agents, *i. e.*, of their oxidation potentials. A ketone high in the series will oxidize rather completely the alcohol corresponding to a ketone low in the series. In such a comparison the quinones will be at the top and the dialkyl ketones at the bottom of the series. For example, diphenoquinone is probably one of the most powerful oxidizing agents among the ketones while di-*i*-propyl ketone is one of the weakest. The quinones have been compared with each other by virtue of the fact that the reduction of a quinone to a hydroquinone is a strictly reversible process, and that an aqueous solution containing appreciable quantities of these two substances, and having a fixed hydrogen-ion concentration, estab-

lishes a definite and accurately determinable potential on a platinum electrode. A comparison of the oxidation potential may be expressed in volts, as for example 0.95 for diphenoquinone, 0.71 for *p*-benzoquinone, 0.48 for α -naphthoquinone and 0.15 for 9,10-anthraquinone.²

The present paper is concerned with the comparison of several ketones which are much weaker as oxidizing agents than the quinones referred to above. It is not possible as yet to express quantitatively their oxidation potentials. It must suffice to state their strength as oxidizing agents in terms of a standard ketone. However, it is hoped that the gap in the series of ketones between the quinones and benzophenone may be bridged by the study of ketones of intermediate oxidation po-

(1) Procter and Gamble Fellow, 1938–1939.

(2) Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 96.