A slurry of 100 g. of silver nitrite and 250 ml. of anhydrous ether in a 500-ml. three-necked flask fitted with a drying tube, dropping funnel and glass paddle stirrer was cooled in a salt–ice-bath and 46.25 g. (0.5 mole) of *t*-butyl chloride was added dropwise over a period of an hour. After stirring at ice temperature for a total of 28 hours, the silver salts were removed by filtration, washed with ether and the washings were added to the green filtrate. The ether solution of products was placed in a flask fitted to a 4-ft. glass helix packed column, the column head being cooled by circulating brine and set for total reflux. Two Dry Ice traps were placed between the head of the column and the vacuum pump. Without application of heat, the pressure was reduced to 200 mm., then to 50 mm. and finally to 10 mm. and distillate was collected until it started to freeze in the first trap as it came over. (The material which had not distilled amounted to 10.53 g. of a blue liquid; it was treated as described below.) The distillate, consisting of ether and nitrite, was diluted to 500 ml. with ether and one ml. of this was further diluted to 50 ml. From the absorbance at 365, 379 and 395 mμ it was found that 32.7 g. of *t*-butyl nitrite (64% yield) had been produced.

Rectification of the diethyl ether–*t*-butyl nitrite solutions manifestly failed to give complete separation. The ether distilling off was yellow and it had a distinct odor of *t*-butyl nitrite. Despite this, there was obtained 20.8 g. (40% yield) of *t*-butyl nitrite, b.p. 63°, n^{20}_D 1.3687.

The 10.53 g. of blue liquid left after *t*-butyl nitrite and diethyl ether were removed from the reaction product (see above) was diluted with an equal volume of 35–37° petroleum ether, washed with water, then with 10% sodium hydroxide until the aqueous layer remained colorless, then with 85% phosphoric acid, and finally with water. After drying over anhydrous magnesium sulfate, the petroleum ether solution was distilled. This gave 2.2 g. (4% yield) of *t*-nitrobutane, b.p. 125–127°, n^{20}_D 1.4022; lit. values[23]: n^{20}_D 1.4015, b.p. 126°.

Duplication of this experiment, except for the addition of 100 g. of Drierite to the reaction mixture, gave a 63% yield of *t*-butyl nitrite and a 5% yield of *t*-nitrobutane.

1-Phenyl-2-nitro-2-nitrosopropane (**1-Phenyl-2-propyl Pseudonitrole**).—An aqueous alkaline solution of 1-phenyl-2-nitropropane containing sodium nitrite was acidified with hydrochloric acid. The product was taken up in diethyl ether, the blue solution was washed with water, dried over anhydrous magnesium sulfate and placed in a refrigerator. The white crystals obtained were recrystallized from a mixture of acetone and ether; m.p. 89–90° (to a blue liquid). *Anal.* Calcd. for $C_9H_{10}N_2O_3$: C, 55.60; H, 5.15; N, 14.43. Found: C, 55.81, 55.68; H, 5.26, 5.33; N, 14.65, 14.28.

LAFAYETTE, INDIANA

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[23] R. H. Wiswall and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reactions of Alkyl Iodides with Halogens[1]

BY F. MARSHALL BERINGER AND HERMAN S. SCHULTZ

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Optically active 2-iodoöctane reacted with chlorine or with bromine in a cold inert solvent to give as a main product 2-chloroöctane or 2-bromoöctane of predominantly inverted configuration. Similar reaction with iodine monochloride yielded predominantly inverted 2-chloroöctane, optically inactive 2,3-dichloroöctane and an optically inactive iodochloroöctane.[2] Under similar conditions neopentyl iodide reacted with chlorine and bromine to give *t*-amyl halides and the halogen adducts of trimethylethylene. Possible mechanisms for these reactions are discussed.

Introduction

Currently it appears that there are three mechanisms by which alkyl halides can exchange with free halogens. First, exchange may be initiated by iodine atoms produced thermally or by photolysis.[3] With allyl iodide another mechanism is apparently operating, namely, coördination of molecular iodine with the olefinic bond followed by loss of a different pair of adjacent iodine atoms.[4] Finally there seems to be a third, non-radical path available for exchange with chlorine, bromine or iodine monochloride.[5-7] It has been suggested[7] that these last exchanges proceed through the formation and breakdown of alkyl iodide–halogen complexes, which may be precipitated at low temperatures[6] and which exist in appreciable amount at room temperature.[8]

TABLE I

REACTIONS OF OPTICALLY ACTIVE 2-IODOÖCTANE: R = 2-OCTYL

Reaction	Conditions	RI	RX[a]	k_1/k_r[b]
RI + Cl_2	1:1 $HCCl_3$–pet. ether,	d_4 1.3164 (26°)	0.8663 (26°)	6.0
↓ 70.6%	−78°, 1.5 hr.; 0°, 1.5 hr.	n_D 1.4877 (22°)	1.4251 (24°)	
RCl + ICl		$[\alpha]_D$ +46.33 (26°)	−24.93 (26°)	
		b.p. 94° (16 mm.)	61° (14 mm.)	
RI + ICl	CCl_4, 25°, 74 hr.	n_D 1.4782 (26°)	1.4224 (23°)	2.1
↓ 33.4%[c]		$[\alpha]_D$ −45.47 (28°)	+12.4 (24°)	
RCl + I_2		b.p. 93 °(16 mm.)	64° (16 mm.)	
RI + Br_2	Pet. ether,	d_4 1.3157 (27°)	1.1010 (26°)	3.5
↓ 85%[d]	−78°, 2 hr. 0°, 1 hr.	n_D 1.4864 (25°)	1.4485 (26°)	
RBr + IBr		$[\alpha]_D$ +45.0 (27°)	−21.0 (26°)	
		b.p. 95° (17 mm.)	79° (17 mm.)	
RI + Br_2	Pet. ether,	n_D 1.4857 (26°)	1.4492 (25°)	2.3
↓ 55%[d]	25°, 5 hr.	$[\alpha]_D$ +45.7 (25°)	−15.4 (25°)	
RBr + IBr		b.p. 72° (5 mm.)	77° (16 mm.)	

[a] X = Cl in reactions with Cl_2, ICl; X = Br in reactions with Br_2. [b] See definition and discussions in footnotes 9 and 10. [c] For other products see Experimental section. [d] Yield was obtained with *dl*-2-iodoöctane.

At the inception of this work in 1950, it was felt that useful information might be obtained concern-

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[1] This paper is taken from the Ph.D. dissertation of Herman S. Schultz, June, 1956. The reaction of optically active 2-iodoöctane with chlorine to give 2-chloroöctane of inverted configuration was reported earlier in the B.S. thesis of David Goland, June, 1951.

[2] The conversion of optically active 2-iodoöctane to 2-chloroöctane of inverted configuration has been independently confirmed recently: E. J. Corey and W. J. Wechter, THIS JOURNAL, **76**, 6040 (1954).

[3] For leading papers see R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 761, 767 (1953).

[4] D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 763 (1953).

[5] A. Geuther, *Ann.*, **123**, 124 (1862); C. Friedel, *ibid.*, **135**, 206 (1865); F. Vlebock and A. Schwappach, *Ber.*, **63B**, 2818 (1930).

[6] J. Thiele and W. Peters, *ibid.*, **38**, 3842 (1905); *Ann.*, **369**, 149 (1909).

[7] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953); **76**, 253 (1954).

[8] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

ing the last class of reactions by studying the reaction of chlorine, of bromine and of iodine monochloride with an optically active secondary alkyl iodide, with the iodide of a hydrocarbon radical susceptible to carbonium ion rearrangement and with a bridgehead 1-iodobicycloheptane or octane. This paper reports the results of the first two structural tests, carried out with optically active 2-iodoöctane and with neopentyl iodide.

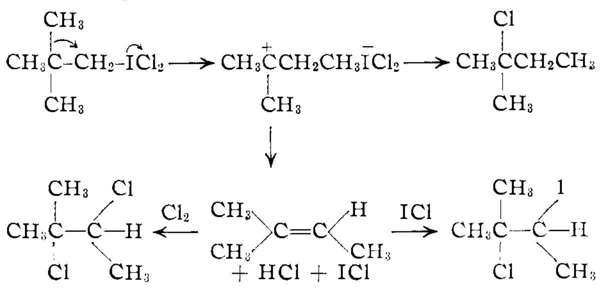
Reactions of 2-Iodoöctane.—Runs in which optically active 2-iodoöctane dissolved in an inert solvent (chloroform, carbon tetrachloride or petroleum ether) was treated at −78° with chlorine or bromine, followed by warming to 0°, and runs in which the compound was treated with iodine monochloride or bromine at 25° all gave as major products 2-chloro- or 2-bromoöctanes with signs of rotation opposite to those of the starting materials. Relevant experimental results are given in Table I.[9–11] Hughes and co-workers[12] have shown that the 2-haloöctanes with the same direction of optical rotation have the same configurations. Thus the present work shows that the replacement of iodine by chlorine or bromine proceeded with predominant inversion of configuration.[2,13] Further, it appears that the reaction with bromine at low temperature was more stereospecific than that at 25°.

The amount of dihalides obtained from such reaction mixtures apparently depended on the halogen and the temperature. None was obtained with chlorine or bromine at −78° and 40% was obtained with iodine monochloride at 25°. Bromine gave an appreciably lower yield of 2-bromoöctane at 25°. The fact that optically active 2-iodoöctane with iodine monochloride gave optically inactive 2,3-dichloroöctane and a related inactive iodochloride suggests that they were formed from 2-octene. Apparently, therefore, the elimination which accompanied replacement followed the Saytzeff rule and may have gone by an ionization type mechanism.[14]

Returning to the main substitution reaction, we might consider briefly the purity of the products. This is especially desirable in view of recent work[15] in which it would be found that the pentanols gave mixtures of isomeric bromopentanes, the proportions of unrearranged and rearranged products depending on the reaction conditions. In the present work 2-octyl tosylate was treated with potassium halides in diethylene glycol at room temperature to give the pure 2-octyl halides. A necessary foundation for the present work, it was found that the infrared spectra of the 2-iodoöctane prepared as above and by Berlak and Gerrard's procedure[11] (using white phosphorus and iodine in carbon disulfide at −15°) were in excellent agreement.[16] Further, the spectrum of the optically active 2-octyl chloride prepared by the reaction of optically active iodide (made by Berlak and Gerrard's procedure[11]) with iodine monochloride compared well with the spectrum of the reference compound.

Reaction of Neopentyl Iodide.—Neopentyl iodide with chlorine at −78° gave *t*-amyl chloride and trimethylethylene dichloride while reaction with bromine gave mainly the analogous dibromo compound plus a small amount of a product that is probably mainly *t*-amyl bromide. As it was shown that *t*-amyl chloride on treatment with chlorine and iodine monochloride gave trimethylethylene dichloride while no reaction occurred with chlorine alone, it may be that the dihalides in the reactions of neopentyl iodide are derived from first formed *t*-amyl halides.

The observation here of another example of the frequently observed rearrangement from a neopentyl to a *t*-amyl system, currently explained as proceeding through electron deficient carbon systems,[17] suggests that the free halogen combines with the bound iodine to give a very electronegative group, presumably $-IX_2$. Ionization of the neopentyl iodosodichloride to a neopentyl cation and the dichloroiodate ion would be accompanied by rearrangement to a *t*-amyl cation and followed by collapse of the ion pair to give *t*-amyl chloride and iodine monochloride[18] or elimination to give trimethylethylene.



Mechanisms for Rearrangement. Elimination and Substitution in the 2-Octyl System.—With only small modifications the mechanisms proposed above for migration of a methyl group in the neo-

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[9] Let $k_1/k_r = X/(1 - X)$. Here $X = {}^1/_2\left[\frac{\alpha\alpha_0^1}{\alpha_0\alpha^1} + 1\right]$. where X is the fraction of octyl bromide or chloride formed with inversion, α is the specific rotation of the bromide or chloride isolated, α_0 is the specific rotation of the pure bromide or chloride, α^1 is the specific rotation of the octyl iodide used, and α_0^1 is the specific rotation of pure octyl iodide.

[10] The values of H. Brauns (*Rec. trav. chim.*, **65**, 799 (1946)) were used in the present work as those of the pure isomers

2-iodoöctane, $[\alpha]^{20}_D$ −47.87, d^{20}_4 vac. 1.4219
2-chloroöctane, $[\alpha]^{20}_D$ −36.15, d^{20}_4 vac. 0.8655
2-bromoöctane, $[\alpha]^{20}_D$ −40.64, d^{20}_4 vac. 1.1055

The preparative method of Brauns is essentially that of Berlak and Gerrard.[11]

[11] M. C. Berlak and W. Gerrard, *J. Chem. Soc.*, 2309 (1949).

[12] E. D. Hughes, F. Jullusburger, S. Masterman, B. Topley and J. Weiss, *ibid.*, 1578 (1935).

[13] Corey and Wechter[2] showed that the rotation of 2-octyl chloride was unaffected by treatment with chlorine under conditions similar to those reported here. Keefer and Andrews[7] showed that isopropyl chloride or *t*-butyl chloride with iodine monochloride in carbon tetrachloride at 25° gave no reaction. Keefer and Andrews[8] also showed that the visible and ultraviolet spectrum of iodine in *t*-butyl chloride is very similar to that of iodine in carbon tetrachloride or heptane.

[14] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 440ff.

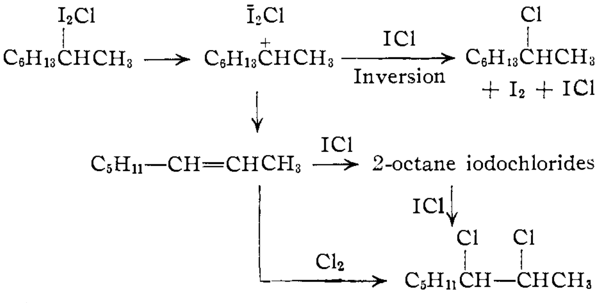
[15] H. Pines, A. Rudin and V. N. Ipatieff, THIS JOURNAL, **74**, 4063 (1952).

[16] The spectrum of 2-iodoöctane prepared by heating the alcohol with red phosphorus and iodine shows the presence of an impurity, probably one or more position isomers. The spectra of the reaction products of this material with chlorine and bromine indicated the presence of impurities in the 2-chloroöctane.

[17] C. K. Ingold, ref. 14, p. 485ff.

[18] If rearrangement did not accompany ionization, then collapse of some of the ion pairs would give neopentyl chloride or bromide; none was found.

pentyl system might seem applicable to the migration of a 3-hydrogen in the 2-octyl system. However, the studies using infrared spectra eliminate the possibility of appreciable migration accompanying the formation of the optically active 2-chloro- and 2-bromoöctanes. The formation of dihalogenoctanes might occur by ionization of 2-octyliodoso iodochloride to the 2-octyl cation and the iodochloroiodate ion ($I\bar{I}Cl$) followed by abstraction of a C_3-hydrogen by the anion to give 2-octene, hydrogen chloride and iodine. Iodine monochloride now might add to the olefin. Further reaction of the iodochloride with iodine monochloride would yield octene dichloride.



There is also the possibility of nucleophilic attack by a halogen molecule on this same ion pair to give 2-chloroöctane. If the ion pair were optically active[19] and attack were from the side opposite the bulky dihalogenoiodate anion, then the 2-chlorooctane or 2-bromoöctane formed would be of inverted configuration, relative to the initial 2-iodooctane. If the ion pairs racemized, then mixtures of both enantiomorphs would result.

A further possible mode of reaction, not involving ionization of the 2-octyliodoso halide, would be nucleophilic attack on this molecule by a halogen molecule leading to 2-chloroöctane or bromoöctane of inverted configuration. No evidence is presently available for the comparative evaluation of this mechanism and one involving prior ionization.

The stereochemical results summarized in Table I were used to calculate k_i/k_r, the ratios of the rates of the reactions with inversion and retention of configuration, in the manner of Corey and Wechter.[2,9]

For the reaction of optically active 2-iodoöctane with chlorine in 1:1 chloroform–petroleum ether at −78° the ratio k_i/k_r was found to have a value of 6.0. This value is somewhat higher than that reported by Corey and Wechter[2] for comparable reactions in pentane (1.6), methylene chloride (1.5), diethyl ether–methylene chloride (1.5) or ethyl acetate (2.3) but is closer to that reported for pyridine–methylene chloride (5.0) and methanol–methylene chloride (5.8). The only solvent in which Corey and Wechter found a higher k_i/k_r ratio was methanol–methylene chloride–4 *M* hydrogen chloride (10.25).

In the present work the k_i/k_r ratio for bromine was found to be 3.5 at −78° and 2.3 at 25°.

Finally, iodine monochloride in carbon tetrachloride showed a k_i/k_r ratio of 2.1 at 25°. Corey and Wechter reported a value of 2.2 for methylene chloride at −70°.

Corey and Wechter[2] have discussed these ratios in terms of the ionizing power of the solvent and the nucleophilicities of the halogens. Until the mechanistic details of these reactions are more firmly established, attempts at further interpretation of these ratios seem premature.

Experimental[20]

Starting Materials.—Chlorine (99.5%, Matheson Chemical Co.), C.P. bromine and C.P. iodine monochloride were used as received. The C.P. chloroform and carbon tetrachloride were dried with phosphorus pentoxide. The petroleum ether, b.p. 28–35°, was treated with concentrated sulfuric acid to remove olefins, washed with water, distilled and stored over anhydrous calcium chloride.

2-Octanol, b.p. 177–179°, was converted with red phosphorus and iodine[21] to 2-iodoöctane, b.p. 95–96° (16 mm.), $n^{22}D$ 1.4883 and $n^{26}D$ 1.4875 in different runs; reported[12] b.p. 95° (16 mm.).

In checking on the possible replacement of secondary aliphatic bromine with chlorine, the 2-bromoöctane used (after purification) was that produced by the reaction of 2-iodoöctane with bromine.

Isomerically pure 2- and 3-chloro- and bromoöctanes and 2-iodoöctane were prepared by adaptations of the procedures used by Pines and co-workers[15] for the preparation of isomerically pure bromopentanes. Merck reagent grade 2-octanol was used, $n^{25}D$ 1.4249. Propionaldehyde and *n*-amylmagnesium bromide gave 3-octanol, b.p. 80–83° (20 mm.), $n^{25}D$ 1.4237–1.4252. In a representative reaction 2-octanol was treated with *p*-toluenesulfonyl chloride in pyridine at 0° to give the tosylate. The crude dry tosylate was shaken for one week at room temperature with four equivalents of potassium bromide in diethylene glycol (b.p. 245–250°). Dilution with water, separation of layers, distillation and fractionation gave a 10.7% yield (based on 2-octanol) of pure 2-bromoöctane, b.p. 78° (16 mm.), $n^{25}D$ 1.4495. Other products were 2-chloroöctane, shaken 7.5 days, 6.2% yield, b.p. 65° (16 mm.), $n^{19}D$ 1.4243; 3-chloroöctane, shaken 9 days, 13.3% yield, b.p. 67.5–68° (20 mm.), $n^{25.5}D$ 1.4244; 3-bromoöctane, shaken 9 days, 34.8% yield, b.p. 81.5° (20 mm.), $n^{25.5}D$ 1.4498–1.4505; 2-iodoöctane, shaken 4 days, 59.3% yield, b.p. 95° (16 mm.), $n^{26.5}D$ 1.4855.

Infrared spectra were taken of these compounds for comparison with other reaction products.

2-Octanol was resolved according to Vogel.[22] Typical physical constants were *l*-2-octanol, b.p. 176–177°, d^{25}_4 0.8152, $[\alpha]^{26}D$ −9.73°.

Optically active 2-iodoöctane was prepared from the *d*- or *l*-2-octanol by treatment with white phosphorus and iodine in carbon disulfide at −15°[11]; physical constants are given in Table I. *dl*-2-Iodoöctane was prepared similarly for comparison of its spectrum to that of iodide prepared by the other methods.

Neopentyl alcohol prepared from trimethylacetic acid[23] was treated with *p*-toluenesulfonyl chloride in pyridine to give **neopentyl tosylate**, m.p. 46.0–46.5°, after crystallization from water–methanol.

Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49; S, 13.23. Found: C, 59.37; H, 7.58; S, 13.55.

The crude dry neopentyl tosylate was treated with two equivalents of sodium iodide in Cellosolve, b.p. 135°, at reflux for two hours. Dilution with water, extraction with petroleum ether, washing with sulfuric acid, and with water followed by distillation gave a 55.2% yield (based on neopentyl alcohol) of **neopentyl iodide**,[24] b.p. 70° (100 mm.),

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[19] See W. von E. Doering and E. Streitweiser, Abstracts of the 119th A.C.S. Meeting, April 1951, p. 45M.

[20] Analyses were performed by Schwarzkopf Laboratories, Woodside, N. Y., or by Weiler and Strauss, Oxford, England.

[21] The method was that reported for *n*-hexadecyl iodide: W. W. Hartman, J. R. Byers and J. B. Dickey, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 322.

[22] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, England, 1948, pp. 489–491.

[23] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[24] The procedure is similar to that briefly mentioned by F. G. Bordwell, B. M. Pitt and M. Knell, *ibid.*, **73**, 5004 (1951).

n^{25}_{D} 1.4858; reported[25] b.p. 70° (100 mm.), n^{21}_{D} 1.4887–1.4890. The product gave no test with silver nitrate.

Anal. Calcd. for $C_5H_{11}I$: C, 30.33; H, 5.60; I, 64.08. Found: C, 30.91; H, 5.55; I, 63.65.

t-Amyl chloride (Eastman Kodak) was redistilled; b.p. 84–85°. Grignard reagents from neopentyl iodide and *t*-amyl chloride on treatment with 1-naphthyl isocyanate gave **N-1-naphthyl-*t*-butylacetamide**, m.p. 167.5–168.0°, and **N-1-naphthylethyldimethylacetamide**, m.p. 139.0–139.5° (reported[26] 137–138°).

Reactions of Alkyl Iodides with Halogens. General Procedure.—2-Iodoöctane and neopentyl iodide were treated with chlorine, bromine and iodine monochloride under conditions summarized in part in Table I and elaborated below. Chlorine was bubbled through a sulfuric acid scrubber and introduced through a sintered glass disk. All reaction mixtures were stirred. Typically, the reaction mixture was shaken with ice-cold aqueous sodium bisulfite, washed with water and dried with anhydrous calcium chloride or magnesium sulfate. Solvent was removed with a Snyder ball column and the residue was distilled, usually under reduced pressure, through a small center-tube column with a Widmer spiral. Distillation at reduced pressure was necessary to avoid decomposition.

2-Iodoöctane with Chlorine.—*dl*-2-Iodoöctane (11.96 g., 49.8 mmoles) dissolved in 50 ml. of chloroform and 50 ml. of petroleum ether was treated at −78° with excess chlorine for 1.5 hours, during which time the reaction mixture darkened. The reaction mixture was allowed to warm to 0° and held at this temperature for 2.5 hours. Standard work-up and distillation gave 5.30 g. (35.7 mmoles, 71%) of **2-chloroöctane**, b.p. 60–61° (14 mm.), n^{24}_{D} 1.4258–1.4282 while 11.92 g. (49.7 mmoles) of 2-iodoöctane in 160 ml. of petroleum ether gave 5.03 g. (33.8 mmoles, 68.2%) of **2-chloroöctane**, b.p. 66.5–67.5° (18–19 mm.), n^{27}_{D} 1.4263.

Anal. Calcd. for $C_8H_{17}Cl$: C, 64.63; H, 11.53. Found: C, 64.51; H, 11.48.

Another run made in petroleum ether gave 4.90 g. of (33.0 mmoles, 66%) 2-chloroöctane, b.p. 61° (14 mm.), n^{24}_{D} 1.4258.

When the reaction was run in petroleum ether at 0° for 1.5 hours, 23.5% of 2-chloroöctane was obtained while 35% of starting 2-iodoöctane was recovered.

A reaction run in chloroform–petroleum ether (as described above) with *d*-(+)-2-iodoöctane gave 70.6% of *l*-(−)-2-chloroöctane; see Table I.

2-Iodoöctane with Iodine Monochloride.—The procedures were similar to those of Keefer and Andrews.[7] ***dl*-2-Iodoöctane** (15.75 g., 65.6 mmoles) was stirred with 21.3 g. (131 mmoles) of iodine monochloride at room temperature (25°) for 87 hours in carbon tetrachloride. Standard work-up and distillation gave 3.10 g. (31.8%) of **2-chloroöctane**, b.p. 66–68° (18 mm.), n^{25}_{D} 1.4247–1.4250, with redistillation at 65.0–65.3° (18 mm.), n^{25}_{D} 1.4259.

Anal. Calcd. for $C_8H_{17}Cl$: C, 64.63; H, 11.53. Found: C, 64.72; H, 11.35

Also collected was 2.18 g. (18.0%) of a substantially pure **dichloroöctane**, b.p. 87–95° (18 mm.), n^{25}_{D} 1.4480. Redistillation for analysis gave material of b.p. 88.5–89.0° (17 mm.), micro b.p. 203°, n^{24}_{D} 1.4500.

Anal. Calcd. for $C_8H_{16}Cl_2$: C, 52.47; H, 8.81. Found: C, 52.28; H, 8.91.

Reported physical constants for 1,2-dichloroöctane[27] are b.p. 67–71° (4 mm.), n^{20}_{D} 1.4531, while those for *erythro*-2,3-dichloroöctane[28] are b.p. 206.1–206.2°, 78° (10 mm.), n^{20}_{D} 1.4523.

The dichloroöctane was shown to be 2,3-dichloroöctane by comparison of the infrared spectrum with those of 2,3-dichloroöctane prepared from octene-2 (95%, from Phillips Petroleum), b.p. 91° (17 mm.), $n^{25.5}_{D}$ 1.4509, and 1,2-dichloroöctane, prepared from octene-1 (99%, from Phillips Petroleum) b.p. 97–98° (16–17 mm.), n^{25}_{D} 1.4513.

There was obtained 3.35 g. (18.6%) of a **chloroiodoöctane**, b.p. 120–126° (18 mm.), n^{25}_{D} 1.5060–1.5090. These higher boiling fractions were reworked by washing with dilute sodium hydroxide and water, drying and redistilling, b.p. 86–87° (2.5 mm.), n^{25}_{D} 1.5070, This material could be kept without substantial decomposition only by refrigeration.

Anal. Calcd. for $C_8H_{16}ClI$: C, 34.99; H, 5.87. Found: C, 35.23; H, 6.06.

A run in petroleum ether at 0° for 2.5 hours gave back 53% of unreacted 2-iodoöctane, while a run at 20° for 30 hours gave back 58%.

***l*-(−)-2-Iodoöctane** reacted with iodine monochloride in carbon tetrachloride substantially as detailed for the *dl*-iodide above. Besides 33.4% of ***d*-(+)-2-chloroöctane** (see Table I) there was obtained 11.2% of 2,3-dichloroöctane, b.p. 88–90° (17 mm.), n^{23}_{D} 1.4478–1.4480, $d^{23.5}_{4}$ 1.0102, optically inactive, and 29.7% of a substantially pure **chloroiodoöctane**, b.p. 85–86° (2 mm.), n^{26}_{D} 1.5032–1.5044, d^{26}_{4} 1.4326, optically inactive (properties as cited after redistillation).

The dichloroöctane product infrared spectrum here too was shown to coincide in all essentials with that of reference 2,3-dichloroöctane and to differ from that of 1,2-dichloroöctane.

2-Iodoöctane with Bromine.—*dl*-2-Iodoöctane and bromine, 50.0 mmoles each, in petroleum ether stirred two hours at −78° and one hour at 0°, gave 8.2 g. (85%) of **2-bromoöctane**, b.p. 77.5–78.0° (16 mm.), $n^{24.5}_{D}$ 1.4490-1.4494. In a similar run, after two hours at −78° the reaction mixture was quenched with 30 ml. of water containing 15 g. of sodium bisulfite. There was obtained 78% of **2-bromoöctane**, b.p. 75–76° (15–16 mm.), n^{23}_{D} 1.4522–1.4500.

Anal. Calcd. for $C_8H_{17}Br$: C, 49.75; H, 8.87. Found: C, 49.69; H, 8.72.

2-Iodoöctane (11.15 g., 46.5 mmoles) with bromine (14.9 g., 93.0 mmoles) in petroleum ether at 25° for 38 hours gave 4.95 g. (25.6 mmoles, 55%) of 2-bromoöctane, b.p. 78.5–79.0° (16 mm.), n^{25}_{D} 1.4506–1.4513, as well as higher boiling material with a higher index of refraction.

d-(+)-2-Iodoöctane with bromine in petroleum ether at −78° and at 25° gave *l*-(−)-2-bromoöctane; see Table I.

2-Bromoöctane was treated with chlorine at −78° in petroleum ether in the standard manner. Almost all the starting material was recovered.

Neopentyl Iodide with Chlorine.—Chlorine was passed for three hours into a solution of neopentyl iodide (40.0 g., 202 mmoles) in petroleum ether at −78°. The reaction flask then was placed in an ice-water bath for 1.5 hours. The usual work-up and distillation gave several main fractions, which were extracted with sulfuric acid, washed with water, dried and redistilled.

The lower boiling fraction was ***t*-amyl chloride**, b.p. 85–86°, n^{25}_{D} 1.4017, yield 27.6%.

Anal. Calcd. for $C_5H_{11}Cl$: C, 56.34; H, 10.40. Found: C, 56.81; H, 10.32.

This product gave an immediate heavy precipitate with silver nitrate. Further, on conversion to the Grignard reagent and treatment with 1-naphthyl isocyanate there was obtained a 1-naphthalide, m.p. 139–139.5°, undepressed by admixture with the naphthalide from authentic *t*-amyl chloride and depressed with the naphthalide of neopentyl iodide; see under "Starting Materials."

The higher boiling fraction was 2,3-dichloro-2-methylbutane, b.p. 65.5–67° (102–103 mm.), n^{25}_{D} 1.4394–1.4410, yield 28%; micro b.p. of n^{25}_{D} 1.4410 material is 129°.

Anal. Calcd. for $C_5H_{10}Cl_2$: C, 42.58; H, 7.15. Found: C, 42.73; H, 7.16.

The structure of 2,3-dichloro-2-methylbutane follows from its chemical properties and reactions. It gave a negative test with alcoholic silver nitrate, formed iodine on treatment with sodium iodide in 2-ethoxyethanol at 135°, and has an infrared spectrum identical in all essentials with that of authentic 2,3-dichloro-2-methylbutane prepared by the addition of chlorine to trimethylethylene (95% pure, kindly supplied by Phillips Petroleum Co.), b.p. 65–66° (99 mm.), n^{25}_{D} 1.4412, micro b.p. 130°. Further treatment of the dichloro compound with powdered zinc and glacial acetic acid to form the olefin, addition of bromine to form the analogous vicinal dibromide and heating of the dibromide with water in a sealed tube at 100° for six hours gave 3-methylbutanone-2 (positive iodoform test). The ketone

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[25] F. C. Whitmore, E. L. Wittle and B. R. Harriman, THIS JOURNAL, **61**, 1585 (1939).

[26] H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2119 (1934).

[27] M. S. Kharasch and A. F. Zarist, *ibid.*, **73**, 964 (1951).

[28] M. C. Haff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3333 (1951).

yielded a 2,4-dinitrophenylhydrazone, m.p. 122.5–123°, undepressed by admixture with an authentic sample.[29] The 2,4-dinitrophenylhydrazone of isovaleraldehyde, m.p. 125.5–126°, strongly depressed the melting point of the above sample.

Neopentyl Iodide with Bromine.—Neopentyl iodide (92.0 mmoles) reacted with bromine (93.3 mmoles) in petroleum ether for 1.25 hours at −78° and 1.5 hours at 0° gave a very small amount (0.57 g., 4%) of an impure low boiling fraction, n^{22}_D 1.4448, b.p. 55–58° (120 mm.), micro b.p. 106°; reported[30] for *t*-amyl bromide, b.p. 108° (765 mm.), n^{20}_D 1.4421. There was not enough to refractionate.

Analysis was obtained on a similar material, probably *t*-amyl bromide, from an earlier run, b.p. 50.5–52° (115 mm.), n^{25}_D 1.4370.

Anal. Calcd. for $C_5H_{11}Br$: C, 39.75; H, 7.34. Found: C, 40.18; H, 7.45.

A higher boiling fraction on refractionation gave 2,3-dibromo-2-methylbutane, b.p. 74–75° (36 mm.), n^{22}_D 1.5020–1.5050, 7.04 g. (33% yield). Analysis was obtained on a similar material from an earlier run, micro b.p. 168–169°, n^{25}_D 1.5000.

Anal. Calcd. for $C_5H_{10}Br_2$: C, 26.11; H, 4.38. Found: C, 26.52; H, 4.32.

The structure was demonstrated by making the 2,4-dinitrophenylhydrazone of 3-methylbutanone-2 formed after first treating the dibromide with water in a sealed tube at 100° for six hours. No depression was obtained either with an authentic sample or with that obtained from the 2,3-dichloro-2 methylbutane (see above).

Reaction of *t*-Amyl Chloride with Chlorine.—*t*-Amyl chloride was chlorinated under the conditions described above for neopentyl iodide with the inclusion of an equivalent of iodine monochloride. Besides 44% of recovered starting material there was obtained 29% of 2,3-dichloro-2-methylbutane, b.p. 60–67° (104 mm.), n^{26}_D 1.4338–1.4415. The infrared spectrum of refractionated material, b.p. 66–67° (102 mm.), n^{26}_D 1.4405, was identical with that of authentic 2,3-dichloro-2-methylbutane (see above) and with the rearrangement product from the reaction of neopentyl iodide and chlorine.

t-Amyl chloride, chlorinated without iodine monochloride, was recovered almost unchanged.

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[29] A similar conversion of 2,3-dibromo-2-methylbutane to 3-methylbutanone-2 has been reported by F. C. Whitmore, W. L. Evers and H. S. Rothrock, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 408.

[30] N. A. Lange, "Lange's Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, Sixth Edition, 1946.

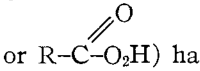
[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. III.[2] Structure of Aliphatic Peracids in Solution and in the Solid State. An Infrared, X-Ray Diffraction and Molecular Weight Study[3]

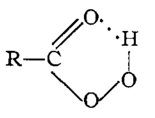
BY DANIEL SWERN, LEE P. WITNAUER, C. ROLAND EDDY AND WINFRED E. PARKER

RECEIVED APRIL 22, 1955

Infrared absorption spectra have been obtained on long-chain aliphatic peracids in solution (C_8–C_{16}) and in the solid state (C_{14}, C_{16}), and X-ray diffraction patterns have been obtained on the solid peracids (C_9–C_{16}). Infrared studies show that in solution the peracids exist exclusively as intramolecularly chelated monomers containing a five-membered ring (I). In the solid state the peracids, like the corresponding *n*-aliphatic acids and alcohols, occur as dimers (II) in which two of the monomer units are linked through intermolecular hydrogen bonds. The dimers, unlike those of the corresponding *n*-aliphatic acids and alcohols, dissociate completely to monomers when they are dissolved in a solvent. Molecular weight determinations in benzene support this last conclusion. In solution, peracids show a broad band of medium intensity at about 865 cm.$^{-1}$ (11.56μ), attributed to skeletal vibrations of the O–O bond. The peracids, unlike the even and odd numbered *n*-aliphatic acids, crystallize with the same end packing and angle of tilt, so that a plot of long spacings against number of carbon atoms yields a single straight line.

Although organic peracids have been known for about fifty years,[4] their structure (usually written as RCO_3H or  $R-\overset{\overset{O}{\|}}{C}-O_2H$) has not been worked out unequivocally. Within the past five years several investigators have applied physical methods, particularly infrared (which has proved to be the most fruitful), to the solution of this problem.[5–11] These workers studied only the lowest aliphatic peracids[7–11] (performic, peracetic, perpropionic and perbutyric acids) and perbenzoic acid.[5,6] The short-chain peracids are corrosive liquids and they are difficult to obtain and keep in a pure state completely free of water, hydrogen peroxide and/or the corresponding carboxylic acid. They are quite unstable (performic acid is explosive[7]) and readily attack the cells used in determining their infrared spectra. Perbenzoic acid although it is a solid which can be readily purified, is a more complicated compound to study because of the absorption characteristics of the phenyl group.

In spite of these difficulties certain conclusions have been reached. Giguère and Olmos[7] reported that performic and peracetic acids exist exclusively as hydrogen bonded, intramolecularly chelated monomeric substances (I), both in the liquid and vapor states. These investigators described an approximate configuration of the percarboxyl group and also gave interatomic distances. The



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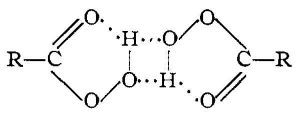

II

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[1] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Part II, THIS JOURNAL, **77**, 4037 (1955).

[3] Presented at the Fall Meeting of the American Chemical Society, Minneapolis, Minn., September 11-16, 1955.

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