TABLE V

PROPERTIES[13] OF *n*-ALKYL HYDROPEROXIDES, ROOH

n-Alkyl group	g.	Yield %	B.p., °C.	Press., mm.	$n^{20}D$	Density, d^{20}_4	M.p., °C.	Formula	Analyses,[c] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Butyl[b]	1.15	42	40–42	8	1.4057	0.907	....	$C_4H_{10}O_2$	53.31	53.30	11.19	11.42
n-Amyl	1.80	43	41–42	4	1.4146	.897	....	$C_5H_{12}O_2$	57.66	57.43	11.61	11.77
n-Hexyl	2.07	44	42–43	2	1.4208	.891	....	$C_6H_{14}O_2$	60.98	60.90	11.94	12.02
n-Heptyl	2.05	38	46–47	0.5	1.4265	.884	−37.5 to −37.0	$C_7H_{16}O_2$	53.59	63.43	12.20	12.21
n-Octyl[a]	2.23	38	54–55	.7	1.4311	.881	−33 to −32	$C_8H_{18}O_2$	65.71	65.83	12.41	12.59
n-Nonyl	2.48	39	53–55	.3	1.4330	.878	−20 to −19	$C_9H_{20}O_2$	67.45	66.86	12.58	12.61
n-Decyl	3.07	45	61–63	.3	1.4378	.871	− 8.5 to −7.5	$C_{10}H_{22}O_2$	68.91	68.89	12.72	12.91

[a] In a similar run a 3-g. sample of crude *n*-octyl hydroperoxide detonated mildly when being distilled at 2 mm. pressure and a bath temperature of 68°. The thermometer was blown from the flask but the flask was not shattered. [b] Reference 7 reports $n^{20}D$ 1.4032, d^{20}_4 0.9078 for *n*-butyl hydroperoxide. [c] Each analysis is the average of two determinations. The maximum deviation from the average in any case was 0.10 and the average deviation was 0.06.

drogen peroxide (40.0 g., 0.35 mole), 50% aqueous potassium hydroxide (10.0 g., 0.089 mole), 130 ml. of methanol and 15 ml. of water at 23–25° for 24 hours was made strongly basic at 0° with 30 g. of 50% aqueous potassium hydroxide. After extraction with hexane, the aqueous layer was brought to *p*H 7 and extracted with six 20-ml. portions of benzene. The alkyl hydroperoxide was taken up in 40 ml. of 25% potassium hydroxide and transferred to ether by neutralizing the mixture and extracting with three 15-ml. portions of ether. The ether was dried over sodium sulfate and distilled to give *n*-heptyl hydroperoxide, 5.79 g., 56% yield, b.p. 45–47° (0.05 mm.).

The hydroperoxides were redistilled, and the physical constants of the purified samples determined. The properties of these purified samples as well as their analyses are shown in Table V. Small quantities of the purified hydroperoxides were heated at 2°/min. in 1.5-mm. Pyrex capillary tubes. Under these conditions the first bubbles of gas appeared at 89 to 92°, and bubbling became fairly steady at 110–115°. No violent decompositions were observed, although the temperature reached 160°. The lower members of the series had boiled out of the capillary before 160°, so the effect of the higher temperature on these hydroperoxides was not established; however, direct flame heating of a capillary tube containing *n*-propyl and *n*-butyl hydroperoxide caused only sputtering of the contents.

All of the hydroperoxides had in common a characteristic sharp odor. The butyl and amyl hydroperoxides caused reddening of the skin and resulted in a severe chemical burn when allowed to stay in contact with the skin. The higher hydroperoxides caused irritation of the skin, but the effects were less severe than those of the *n*-butyl and *n*-amyl homologs.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

Organic Peroxides. II. Secondary Alkyl Hydroperoxides

BY HOMER R. WILLIAMS AND HARRY S. MOSHER

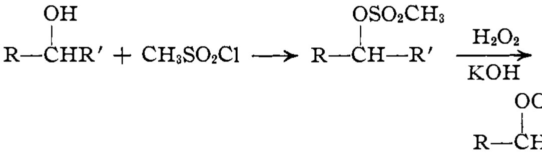
RECEIVED JANUARY 18, 1954

A series of saturated secondary alkyl hydroperoxides has been prepared by the reaction of secondary alkyl methanesulfonates with alkaline hydrogen peroxide in aqueous methanol. Compared with other methods the yields are satisfactory (20–25%) and the application of this method makes potentially available a wide variety of alkyl hydroperoxides previously inaccessible.

Criegee[1] has recently reviewed the methods for synthesis of hydroperoxides. Two of these, the air-oxidation of hydrocarbons and the action of dialkyl sulfates on hydrogen peroxide in the presence of base (the method of Baeyer and Villiger) have been applied successfully to the preparation of saturated secondary alkyl hydroperoxides. For example 2-heptyl hydroperoxide has been reported to result by the air-oxidation of *n*-heptane[2] and cyclohexyl hydroperoxide has been isolated from the air-oxidation of cyclohexane.[3]

The method of Baeyer and Villiger has been used for the preparation of isopropyl hydroperoxide[4] and for *s*-butyl hydroperoxide.[5] In addition to these methods reviewed in Criegee,[1] Walling and Buckler[6] have recently reported the preparation in good yield of several hydroperoxides by low temperature air-oxidation of Grignard reagents. This method is applicable to primary, secondary and tertiary alkyl hydroperoxides.

The recently reported method for the preparation of *n*-alkyl hydroperoxides from alkyl methanesulfonates and hydrogen peroxide[7] has now been extended to include saturated secondary alkyl hydroperoxides.



$$R\text{—}\overset{OH}{\overset{|}{C}}HR' + CH_3SO_2Cl \longrightarrow R\text{—}\overset{OSO_2CH_3}{\overset{|}{C}H}\text{—}R' \xrightarrow[KOH]{H_2O_2} R\text{—}\overset{OOH}{\overset{|}{C}H}\text{—}R'$$

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[1] R. Criegee, "Methoden der Organischen Chemie, Vierte Auflage," Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, pp. 9–61.

[2] K. I. Ivanov, V. K. Sovinova and V. P. Zhakhovskaya, *Doklady Akad. Nauk. S. S. S. R.*, **72**, 903 (1950); *C. A.*, **44**, 8316 (1950). The yield was 0.5–0.6% by titration; the isolated yield was not given.

[3] S. A. Farkas and A. Passaglia, THIS JOURNAL, **72**, 3333 (1950). The yield by titration was 1.9% of the cyclohexane taken and of this 38.3% was isolated in purified form.

[4] (a) S. S. Medvedev and E. N. Alexejeva, *Ber.*, **65B**, 133 (1932). A 50% yield was reported in solution by titration but the amount of isolated material was not reported. (b) W. Eggersglüss, "Organische Peroxyde," Verlag Chemie, G.m.b.h., Weinheim, 1950, p. 79, reports an 11% yield of pure isopropyl hydroperoxide by this method.

[5] E. G. Lindstrom, THIS JOURNAL, **75**, 5123 (1953). The yield of isolated *s*-butyl hydroperoxide was 40% based on 2-butyl sulfate which reacted.

[6] C. Walling and S. A. Buckler, *ibid.*, **75**, 4373 (1953). See also J. Schmidlin, *Ber.*, **39**, 631, 4184 (1909).

[7] H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2984 (1954).

TABLE I

YIELDS AND PROPERTIES OF ALKYL METHANESULFONATES

Alkyl group	Yield		B.p.,	Press.,			Analyses,[b] % Carbon		Hydrogen	
	Wt., g.	%	°C.	mm.	$n^{20}\text{D}$	Formula	Calcd.	Found	Calcd.	Found
2-Butyl	20.65	67	49	1	1.4252	$C_5H_{12}SO_3$	39.47	39.46	7.95	7.95
Isobutyl[d]	22.60	74	53	1	1.4245	$C_5H_{12}SO_3$	39.47	39.55	7.95	7.85
2-Pentyl[d]	23.70	71	63–64	0.5	1.4304	$C_6H_{14}SO_3$	43.36	43.12	8.49	8.57
3-Pentyl	25.25	76	53–54	0.4	1.4315	$C_6H_{14}SO_3$	43.36	42.98	8.49	8.64
Isoamyl[d]	27.60	83	56–57	0.5	1.4288	$C_6H_{14}SO_3$	43.36	43.56	8.49	8.63
Cyclopentyl	20.00	60[a]	71–73	1	1.4570	$C_6H_{12}SO_3$	43.90	43.88	7.37	7.51
2-Hexyl[d]	29.50	81	60–61	0.5	1.4322	$C_7H_{16}SO_3$	46.65	46.65	8.95	9.00
3-Hexyl	27.70	78	54–57	0.5	1.4338	$C_7H_{16}SO_3$	46.65	46.27	8.95	8.57
2-Heptyl[d]	28.30	70	66–67	0.5	1.4342	$C_8H_{18}SO_3$	49.47	49.27	9.34	9.41
4-Heptyl[d]	17.60	43[a]	78–80	2	[c]					
2-Octyl[d]	33.80	81	78–80	0.5	1.4266	$C_9H_{20}SO_3$	51.90	51.84	9.68	9.61

[a] These low yields resulted from decomposition of part of the material during distillation. [b] Analysis by Microchemical Specialties Co., Berkeley, Calif. [c] Material was not pure and physical properties therefore not recorded. [d] These alkyl methanesulfonates were stored for extended periods over powdered sodium bicarbonate without decomposition.

The reaction conditions used for the preparation of the secondary alkyl hydroperoxides were essentially the same as reported for the normal series.[8] The rate of the reaction of secondary alkyl sulfonates as measured by the rate of disappearance of base from the reaction mixture (Table III), was slower than for the straight-chain normal alkyl sulfonates. The yields of hydroperoxides, along with the conditions for the reaction and the physical properties of the products, are given in Table I. It seems evident that the best yields are obtained when the hydroperoxy group is on the second carbon atom while the yields fall off if both groups attached to the carbinol carbon atom are ethyl or larger. This is illustrated in the case of 4-heptyl methanesulfonate; potassium hydroxide disappeared from the reaction mixture at about the same rate as in the case of the isomeric 2-heptyl methanesulfonate but only a trace of hydroperoxide was isolated and a fair amount of an alkene was formed instead. If it is assumed that there are three competing reactions: (1) the desired alkylation of hydrogen peroxide which takes place by a bimolecular displacement reaction, (2) basic hydrolysis of the alkyl methanesulfonate, and (3) a second-order elimination reaction which leads to the olefin, then one would expect that any hindrance to back-side attack would retard the desired S_N2 reaction. It is therefore not surprising that the yields in the reaction of secondary alkyl sulfonates (up to 25%) are less than found for the normal straight chain alkyl sulfonates (34–55%). One would also expect approximately the same yield from reactants having comparable steric hindrance. The experimental results reported in Table I are in agreement with these assumptions. Two branched primary alkyl methanesulfonates were prepared, isoamyl and isobutyl. The former was converted into the hydroperoxide in good yield but the latter gave only traces of isobutyl hydroperoxide. The results are in accord with the known inert character of isobutyl halides in S_N2 displacement reactions.

The secondary alkyl methanesulfonates were prepared from the corresponding secondary alcohols by reaction with methanesulfonyl chloride in the presence of pyridine.[8] Unlike the primary alkyl methanesulfonates, many of the secondary compounds were unstable and decomposed autocatalytically to give the olefin and methanesulfonic acid. Prolonged heating initiated this decomposition but it was possible to distil all of the compounds which were prepared in small quantities (10–15 g.) from finely divided calcium carbonate without decomposition. Most of the secondary alkyl methanesulfonates would completely decompose in a few days or weeks unless stored over sodium bicarbonate. Under these conditions most of the secondary alkyl methanesulfonates were reasonably stable.

Molecular Refractions.—The molecular refractions for the fourteen alkyl hydroperoxides reported in Table VI have been calculated from the Lorenz–Lorentz equation. The difference in the calculated values and the theoretical contribution of the carbon hydrogen portion of the molecule gives a value for the molecular refraction of the hydroperoxy group, -OOH. The average of molecular refraction for the -OOH group in these fourteen examples was $[n]\text{D}$ 4.73 with an average deviation of 0.12. Rieche[9] has reported a value of 3.7 for the molecular refraction contribution of the -O-O- portion of the molecule in hydroperoxides based on his data for methyl and ethyl hydroperoxides. The contribution of the -O-O- group to the molecular refraction of the molecule, based on the fourteen examples in Table VI, is 3.64. Milas[10] has reported a value of 2.19 for the contribution of the "peroxidic oxygen" toward the molecular refraction of hydrogen peroxide and this value has been shown to correlate satisfactorily with a series of hydroperoxides.[10] The average value for the molecular refraction contributions for the "peroxidic oxygen" based on the fourteen examples of alkyl hydroperoxides in Table VI is 2.11. There does not seem to be any systematic deviation within this series.

Acknowledgment.—We wish to thank the California Research Corporation for a grant and fellowship support which made these studies possible.

Experimental

The Preparation of Alkyl Methanesulfonates.—The secondary alkyl methanesulfonates were prepared with the following modifications by the method reported by Sekera

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(8) V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

(9) A. Rieche, "Alkyl Peroxyde and Ozonide," Verlag von T. Steinkopff, Dresden and Leipzig, 1931, p. 100.

(10) N. A. Milas, D. A. Surgenor and L. H. Perry, THIS JOURNAL, **68**, 1617 (1946).

TABLE II

YIELDS AND PROPERTIES OF ALKYL HYDROPEROXIDES

Alkyl group	Yield Wt., g.	Yield %	B.p., °C.	Press., mm.	$n^{20}D$	Density d^{22}_4	Formula	Analyses,[a] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Butyl[b]	1.42	19.5	41–42	11	1.4050	0.907	$C_4H_{10}O_2$	53.31	53.21	11.19	11.26
2-Pentyl	1.71	20.8	46–47	7	1.4140	0.899	$C_5H_{12}O_2$	57.66	57.40	11.61	11.73
3-Pentyl	1.42	17.0	51–52	10	1.4155	0.909	$C_5H_{12}O_2$	57.66	57.57	11.61	11.61
Isoamyl	4.35	52.0	47–48	6	1.4118	0.890	$C_5H_{12}O_2$	57.66	57.43	11.61	11.58
Cyclopentyl	1.68	20.9	46–47	4	1.4533	1.026	$C_5H_{10}O_2$	58.80	59.06	9.87	9.90
2-Hexyl	2.44	25.6	29–30	1	1.4186	0.886	$C_6H_{12}O_2$	60.98	60.95	11.94	11.91
3-Hexyl	0.86	9.0	48–50	5	1.4204	0.893	$C_6H_{12}O_2$	60.98	61.20	11.94	12.15
2-Heptyl[d]	2.69	25.7	32–33	0.5	1.4237	0.879	$C_7H_{16}O_2$	63.59	63.83	12.20	12.49
4-Heptyl	Trace	..	...	..	....	...	.....	...	...	...	...
2-Octyl[c]	1.90	11.3	58–59	0.4	1.4280	0.878	$C_8H_{18}O_2$	65.71	66.12	12.41	12.35

[a] Analysis by Microchemical Specialties Co., Berkeley, Calif. [b] Ref. 5 reports for 2-butyl hydroperoxide: $n^{20}D$ 1.4052, d^{20}_4 0.9094. [c] Ref. 6 reports for 2-octyl hydroperoxide: b.p. 58–59° (0.5 mm.), $n^{25}D$ 1.4269, d^{20}_4 0.868. [d] Ref. 4a reports for 2-heptyl hydroperoxide: b.p. 38° (0.08 mm.) $n^{20}D$ 1.4305, d^{20}_4 0.9072. These properties do not correspond very closely to those reported in the above table. Since the compound reported in reference 4a was obtained by air-oxidation of *n*-heptane, it very likely is contaminated with isomeric hydroperoxide.

and Marvel[8] for the preparation of *n*-butyl methanesulfonate and described in detail in the first paper of this series.[7] The ether from the ether extract of the alkyl methanesulfonate was removed under reduced pressure at room temperature, and the residue was distilled at the lowest possible pressure to minimize decomposition. Except for 2-butyl, 2-pentyl and 3-pentyl methanesulfonates, the secondary methanesulfonates were distilled in two portions to avoid prolonged heating. In all cases the distillations were made in the presence of 0.5 g. of calcium carbonate. When decomposition occurred during distillation, a rapid evolution of gas and a darkening of the residue occurred, and in no case was it possible to obtain the product after this was observed. When it was necessary to discontinue a distillation before completion, the vacuum was broken only after the distillation flask was removed from the oil-bath and cooled. The experimental data are summarized in Table II.

The Relative Rates of Reaction of Some Alkyl Methanesulfonates with Hydrogen Peroxide and Methanolic Potassium Hydroxide.—The relative reactivities of the three isomeric butyl and heptyl methanesulfonates were compared

TABLE III

THE RELATIVE REACTION RATES OF ISOMERIC BUTYL METHANESULFONATES[a]

	n-Butyl Base remaining, %			*s*-Butyl Base remaining, %			Isobutyl Base remaining, %	
Time, hr.	Presence of H_2O_2	Absence of H_2O_2	Time, hr.	Presence of H_2O_2	Absence of H_2O_2	Time, hr.	Presence of H_2O_2	Absence of H_2O_2
0.0	100	100	0.0	100	100	0.0	100	100
1.2	55	85	1.3	63	79	1.2	94	99
3.4	33	71	3.2	40	58	3.1	89	98
5.3	24	63	5.2	29	49	5.1	87	96
19.1	6	35	18.9	8	28	18.9	66	89

[a] The composition of the reaction mixtures in the presence of H_2O_2 was as follows: methanesulfonate, 1.22 g.; 50% KOH, 1.00 g.; methanol, 5 ml.; 30% H_2O_2, 4.0 g. The runs in the absence of H_2O_2 were the same except that the 4.0 g. of 30% H_2O_2 was replaced with 3.0 g. of H_2O. The temperature was 25–27°.

TABLE IV

THE RELATIVE REACTION RATES OF ISOMERIC HEPTYL METHANESULFONATES[a]

	n-Heptyl Base remaining, %		2-Heptyl Base remaining, %		4-Heptyl Base remaining, %	
Time, hr.	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2
0.0	100	100	100	100	100	100
2.2	65	94	79	90	77	84
4.2	50	88	68	79	64	76
7.4	35	80	52	71	44	64
18.3	17	63	27	58	15	40

[a] The composition of the reaction mixtures in the presence of H_2O_2 was as follows: heptyl methanesulfonate, 1.30 g.; 50% KOH, 0.83 g.; methanol, 11 ml.; H_2O 1.3 ml.; 30% H_2O_2, 3.30 g. The runs in the absence of H_2O_2 had the same composition except the 3.30 g. of H_2O_2 was replaced with 3.0 g. of H_2O. The temperature was held at 24–26°.

TABLE V

REACTION PROPORTIONS IN THE PREPARATION OF ALKYL HYDROPEROXIDES[a]

Methanesulfonate alkyl group	Methanol, ml.	Water, ml.	Time, hr.	Methanesulfonate alkyl group	Methanol, ml.	Water, ml.	Time, hr.
2-Butyl	50	0	20	2-Hexyl	90	10	20
2-Pentyl	80	7	20	3-Hexyl	90	10	20
3-Pentyl	80	7	20	2-Heptyl	125	10	24
Isoamyl	80	7	20	4-Heptyl	125	10	20
Cyclopentyl	80	7	20	2-Octyl	180	14	40

[a] In each case 0.08 mole of alkyl methanesulfonate was treated 10 g. (0.090 mole) of 50% potassium hydroxide solution and 40 g. (0.35 mole) of 30% hydrogen peroxide solution.

TABLE VI

MOLECULAR REFRACTIONS OF HYDROPEROXIDES[a,b]

Alkyl hydroperoxides	MR_D Obsd.	MR_D Calcd.	MR_D carbon–hydrogen contribution (calcd.)	MR_D contribution of hydroperoxy group (calcd.)	Dev. from av.
n-Butyl	24.37	24.36	19.63	4.74	− 0.01
n-Amyl	29.06	28.99	24.26	4.80	− .07
n-Hexyl	33.61	33.63	28.90	4.71	+ .02
n-Heptyl	38.36	38.16	33.43	4.93	+ .20
n-Octyl	42.93	42.89	38.16	4.77	+ .04
n-Nonyl	47.45	47.53	42.80	4.65	− .08
n-Decyl	52.49	52.16	47.43	5.06	+ .33
2-Butyl	24.34	24.33	19.64	4.70	− .03
2-Pentyl	28.80	28.99	24.26	4.54	− .19
3-Pentyl	28.60	28.99	24.26	4.34	− .39
2-Hexyl	33.66	33.63	28.90	4.76	+ .03
3-Hexyl	33.50	33.63	28.90	4.60	− .13
2-Heptyl	38.36	38.16	33.43	4.93	+ .20
2-Octyl	42.86	42.89	38.16	4.70	− .03

[a] Calculated on the basis of 4.634 for the CH_2 group in alcohols, 1.092 for the extra hydrogen atoms, and 4.730 for the hydroperoxide group. [b] All values calculated from data in Table I of this paper or Table V of ref. 7. Refractive indices are with D-line of sodium at 20°.

by titrating aliquots of the reaction mixtures with hydrochloric acid over a period of approximately 20 hours. These data are compared in Tables III and IV with the relative rates of disappearance of base from the reaction mixtures which are comparable in all other respects except that the hydrogen peroxide has been omitted.

The Preparation of Secondary Alkyl Hydroperoxides and Isoamyl Hydroperoxide.—The secondary alkyl hydroperoxides were prepared under conditions similar to those employed for the preparation of the primary isomers[7]; however, the isolation procedure was modified slightly. The preparations were conducted on a larger scale because of the lower yield of hydroperoxides from secondary alkyl methanesulfonates as compared to the primary isomers.

A one-phase reaction mixture was prepared by adding 10.0 g. (0.090 mole) of 50% aqueous potassium hydroxide to a chilled solution consisting of 40 g. (0.35 mole) of 30% hydrogen peroxide, 0.080 mole of the alkyl methanesulfonate, water and methanol as indicated in Table V. The mixture was then placed in a water-bath at room temperature for the period indicated in Table V. After standing at room temperature, the mixture was cooled in ice and combined with 30 g. of 50% potassium hydroxide. The alkaline solution was extracted with 50 ml. of hexane and then neutralized with hydrochloric acid while being cooled in ice.

The neutralized solution was extracted with six 20-ml. portions of benzene which were combined and extracted with 40 g. of 25% potassium hydroxide. The 2-octyl hydroperoxide was extracted with 80 g. of 12% potassium hydroxide because of the formation of a greasy precipitate in the more concentrated solution. The alkaline solution was neutralized with concentrated hydrochloric acid, with cooling, and the liberated hydroperoxide was extracted with three 15-ml. portions of ether. The ether solution was dried over sodium sulfate, freed of ether under aspirator pressure and then distilled at reduced pressure. The yields, properties and analyses are compiled in Table I.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity. IX. A Study of the Aminolysis of Esters of Trichloro- and Trifluoroacetic Acids

BY MADELEINE M. JOULLIÉ AND ALLAN R. DAY

RECEIVED JANUARY 6, 1954

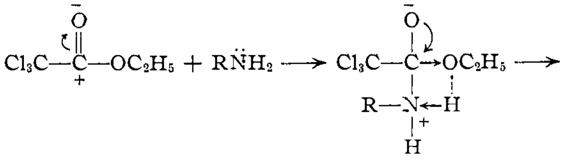
It has been found that esters of trichloroacetic acid and trifluoroacetic acid react in distinctly different ways with primary amines and with secondary amines. With primary amines, cleavage of the carbon–oxygen bond occurs giving the typical end products of an aminolysis reaction, namely, an amide and an alcohol. When 1,2-diamines were used, the ethyl ester of trichloroacetic acid formed derivatives of dihydroimidazole. Ethyl trifluoroacetate, however, reacted with 1,2-diamines to form only the diamide, no dihydroimidazole being formed. Secondary amines reacted with the esters of both trichloroacetic acid and trifluoroacetic acid to give typical haloform reactions. In these cases a carbon–carbon bond was cleaved to form a haloform and a urethan. Mechanisms have been proposed to account for the different behaviors of primary and secondary amines in these reactions.

The cleavage of esters of trichloroacetic acid with alkoxides to form chloroform and alkyl carbonates was reported in 1931.[1] This reaction is very similar to the haloform reaction and probably follows a similar mechanism.

Other anionic reagents, with few exceptions, have not been studied. Concentrated aqueous ammonia converts ethyl trichloroacetate to trichloroacetamide in poor yields.[2] The fact that no chloroform was reported is somewhat surprising since the trichloromethyl group would be expected to cleave very readily. In view of this apparent anomaly, it was decided to study the reactions of ammonia, primary amines and secondary amines with esters of trihalogen substituted acetic acids.

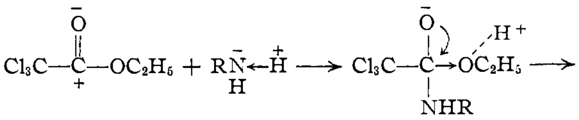
When ethyl trichloroacetate in dry ethanol was treated with dry ammonia, good yields of trichloroacetamide were obtained. Primary amines under anhydrous conditions behaved similarly and formed N-alkyl trichloroacetamides in good yields. If the trichloromethyl group had cleaved, chloroform and a substituted urethan would have been formed but these products were not found. The course of these reactions was not changed by the presence of strong base catalysts such as the ethoxide ion. It would appear that as long as two hydrogen atoms are attached to the nitrogen of the amine, aminolysis of the ester group occurs as the only reaction.

Two possible mechanisms may be written for the reaction with primary amines.



$$Cl_3C-\overset{\bar{O}}{\underset{+}{C}}-OC_2H_5 + R\ddot{N}H_2 \longrightarrow Cl_3C-\overset{\bar{O}}{\underset{R-\overset{+}{N}H_2}{C}}\rightarrow OC_2H_5 \longrightarrow$$

$$Cl_3CCONHR + C_2H_5OH \quad (I)$$

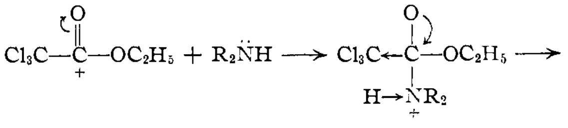


$$Cl_3C-\overset{\bar{O}}{\underset{+}{C}}-OC_2H_5 + R\overset{-}{N}\leftarrow\overset{+}{H}H \longrightarrow Cl_3C-\overset{\bar{O}}{\underset{NHR}{C}}\rightarrow OC_2H_5 \;{}^{H^+} \longrightarrow$$

$$Cl_3CCONHR + C_2H_5OH \quad (II)$$

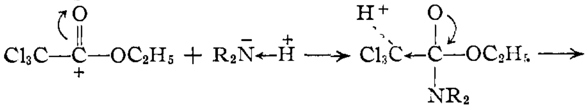
The two mechanisms are very similar, differing only in the time at which the proton is transferred.

Secondary amines reacted with ethyl trichloroacetate in a different manner, giving a typical haloform cleavage with the formation of chloroform and a N-substituted urethan. Here again two possible mechanisms may be written.



$$Cl_3C-\overset{\bar{O}}{\underset{+}{C}}-OC_2H_5 + R_2\ddot{N}H \longrightarrow Cl_3C\leftarrow\overset{\bar{O}}{\underset{H\rightarrow\overset{+}{N}R_2}{C}}-OC_2H_5 \longrightarrow$$

$$CHCl_3 + R_2NCOOC_2H_5 \quad (III)$$



$$Cl_3C-\overset{\bar{O}}{\underset{+}{C}}-OC_2H_5 + R_2\overset{-}{N}\leftarrow\overset{+}{H} \longrightarrow \overset{H^+}{Cl_3C}\leftarrow\overset{\bar{O}}{\underset{NR_2}{C}}-OC_2H_5 \longrightarrow$$

$$CHCl_3 + R_2NCOOC_2H_5 \quad (IV)$$

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(1) H. Meerwein and H. Sönke, *Ber.*, **64**, 2375 (1931).

(2) M. A. Clermont, *Compt. rend.*, **133**, 737 (1901).