while no analogous reaction path is open to the isopropyl radical. Although they give no data in regard to the lifetime of the radicals, Durham, Martin and Sutton[7] indicate a partial decomposition of propyl radical in the vapor phase at 400°.

TABLE I

PRODUCTS OF THE THERMAL EXCHANGE OF IODINE AND THE ALKYL IODIDES

Exchange, %	Total org. activity, c./m.	Per cent. activity as CH_3I	C_2H_5I	i-C_3H_7I	n-C_3H_7I	CH_2I_2
Ethyl iodide (75°, 0.024 M in I_2)						
71	885	0[b]	>98	0[b]	0[b]	0[b]
n-Propyl iodide (75°, 0.024 M in I_2)						
64	660	0[b]	0[b]	0[c]	>98	..[a]
n-Propyl iodide (95°, 0.0008 M in I_2)						
71	5730	0.5	0.2	0.3	98.5	0.5
Isopropyl iodide (95°, 0.0023 M in I_2)						
98	14100	0.0[d]	0.4	98.6	0.7	0.3

[a] No carrier methylene iodide added. [b] < 0.5%. [c] < 1%. [d] < 0.1%.

The results of Table I represent an upper limit to systematic errors that can affect the validity of the present separation methods. It is indicated that the reliability of results obtained by this method is better than a fraction of one per cent., or the limit of the activity measurements should this be higher. Detection of the formation of small amounts of radicals appears to be quite practicable especially in the case of methyl since methyl iodide is easily separated from the higher boiling components.

Further investigations are in progress utilizing the technique described above in studies of alkyl iodide systems.

DEPARTMENT OF CHEMISTRY
CANISIUS COLLEGE
BUFFALO, NEW YORK

A New Synthesis of Aminomalonic Acid[1]

BY JAN H. R. BEAUJON AND WALTER H. HARTUNG

RECEIVED NOVEMBER 26, 1952

Aminomalonic acid was first described in 1864, by Baeyer who prepared it by reduction of potassium oximinomalonate with sodium amalgam and water.[2] Ruhemann and Orton[3] synthesized aminomalonic acid from nitromalonamide by reducing the nitro group with sodium amalgam and water, and removing the amido groups by hydrolysis. Lütz,[4] in 1902, found that he could obtain aminomalonic acid by treating halogenated malonic acid with ammonia. Finally, in 1904, Piloty and Finckh[5] obtained aminomalonic acid by alkaline hydrolysis of uramil, 5-aminobarbituric acid.

In view of the known instability of malonic acids, it is doubtful that any of these methods yields aminomalonic acid in pure form. In most cases the reagents used are quite destructive and the decomposition products, mainly glycine, may be expected to contaminate the product.

The present synthesis employs diethyl carbobenzyloxyaminomalonate, an intermediate in the preparation of malonic acid analogs of α-amino acids.[6] The unsubstituted ester, hydrolyzed under conditions previously described,[6] gives good yields of the alkali salt of carbobenzyloxyaminomalonic acid, which, on catalytic hydrogenolysis in aqueous solution, gives the salts of aminomalonic acid.

Experimental

Potassium Carbobenzyloxyaminomalonate.—This compound was prepared by hydrolysis of 12.4 g. (0.04 mole) of diethyl carbobenzyloxyaminomalonate[6] in 50 ml. of a 20% solution of potassium hydroxide in 95% ethanol. A gummy precipitate, weighing more than 12.5 g. (calcd. for pure dipotassium salt, 12.6 g.), was formed on standing overnight. This precipitate, on attempted recrystallization from 80–90% ethanol, formed a slightly yellowish, oily material. On washing with 95% ethanol it became almost colorless, and after drying over phosphorus pentoxide it turned into a white, hygroscopic solid. *Anal.* Calcd. for $C_{11}H_9O_6NK_2$: N, 4.26. Found: N, 4.31, 4.43.

Potassium carbobenzyloxyaminomalonate could be acidified to produce carbobenzyloxyaminomalonic acid, m.p. 147–148° (uncor.), with evolution of gas. *Anal.* Calcd. for $C_{11}H_{11}O_6N$: N, 5.54. Found: N, 5.56, 5.51.

Monodecarboxylation of carbobenzyloxyaminomalonic acid by boiling with dilute hydrochloric acid yielded N-carbobenzyloxyglycine, m.p. 119–120° (uncor.), m.p. reported, 120°.[7] Although the analysis for the free acid is satisfactory, the visible evolution of gas on its formation suggests that it is more stable as a salt.

Monopotassium Carbobenzyloxyaminomalonate.—To a solution of 2.4 g. of KOH (0.041 mole) in 10 ml. of water was added with constant stirring 10.2 g. of carbobenzyloxyaminomalonic acid (0.04 mole). To the resulting clear solution was added with stirring commercial absolute ethanol until no further precipitate formed. The solid was removed, washed with 95% alcohol and recrystallized three times from 80–90% alcohol; obtained 7.1 g. of pure white crystals, 61.1%. *Anal.* Calcd. for $C_{11}H_{10}O_6NK$: N, 4.82. Found: N, 4.82, 4.85.

Monopotassium Aminomalonate.—A solution of 5.8 g. of monopotassium carbobenzyloxyaminomalonate (0.02 mole) in 50 ml. of distilled water was hydrogenated in the Parr apparatus in the presence of 2 g. of palladium–charcoal catalyst at an initial pressure of 4 atm. hydrogen; shaking was continued for an hour after the gage pressure became constant. The catalyst was removed and the solution concentrated under reduced pressure to 25 ml. and then poured into 150 ml. of boiling absolute ethanol and filtered. The solution, after standing for about a week, yielded large crystals, which were removed and recrystallized twice from 80–90% alcohol; yield 1.0 g., 32%. *Anal.* Calcd. for $C_3H_3O_4NK$: N, 8.91. Found: N, 8.92, 8.86.

Hydrogenation of dipotassium carbobenzyloxyaminomalonate under similar conditions, and isolation of the product as described above, also leads to the monopotassium aminomalonate, the carbon dioxide liberated during hydrogenolysis of the carbobenzyloxyl group accounting for the other potassium ion.

(1) No. 13 in amino acid series. For No. 12 see J. H. R. Beaujon, W. R. Straughn, Jr., and W. H. Hartung, *J. Am. Pharm. Assoc.*, **41**, 581 (1952).

(2) A. Baeyer, *Ann.*, **131**, 291 (1864).

(3) S. Ruhemann and K. J. P. Orton, *J. Chem. Soc.*, **67**, 1002 (1895).

(4) O. Lütz, *Ber.*, **35**, 2549 (1902).

(5) O. Piloty and C. Finckh, *Ann.*, **333**, 71 (1904).

(6) J. H. R. Beaujon and W. H. Hartung, *J. Am. Pharm. Assoc.*, **41**, 578 (1952).

(7) H. D. Carter, R. L. Frank and H. W. Johnston, *Org. Syntheses*, **23**, 13 (1943).

SCHOOL OF PHARMACY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

4-Nitrophthalimides. I. Derivatives of Alkyl Halides Giving a Saponification Equivalent[1]

BY JOHN H. BILLMAN AND R. VINCENT CASH

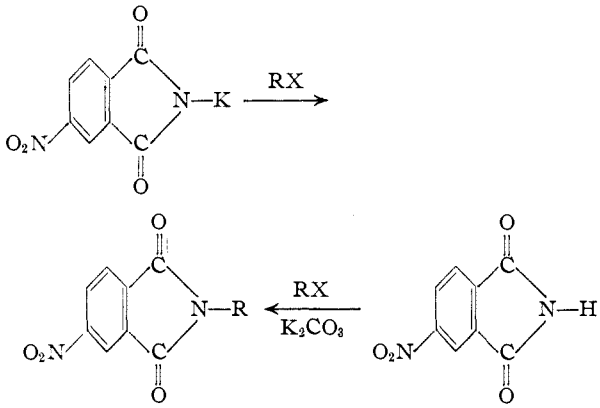
RECEIVED NOVEMBER 8, 1952

Among the many derivatives suggested for the identification of alkyl halides are the N-alkyl-

(1) From the Ph.D. Thesis of R. Vincent Cash, Indiana University, September, 1951.

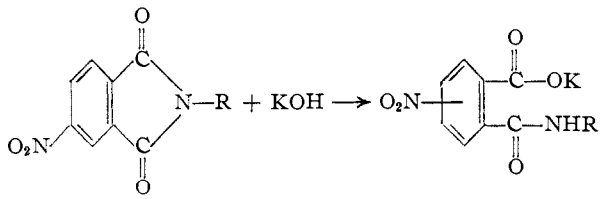
phthalimides,[2] the N-alkyl-3-nitrophthalimides,[3] the N-alkyltetrachlorophthalimides[4] and the related N-alkylsaccharins.[5] In terms of suitability, each of these derivatives has certain limitations—the N-alkylphthalimides and the N-alkylsaccharins are rather low-melting and may separate as oils, the N-alkyl-3-nitrophthalimides and the N-alkyltetrachlorophthalimides give higher melting points but require 10 hours of heating for their preparation.

The possibility of the N-alkyl-4-nitrophthalimides as derivatives of alkyl halides has been investigated. The imides which we prepared may be obtained by the reaction of the proper alkyl halide with either potassium 4-nitrophthalimide or 4-nitrophthalimide and potassium carbonate. High



yields are obtainable by either reaction, in dimethylformamide, according to the directions which follow. The latter reaction is more convenient since it obviates the preparation of potassium 4-nitrophthalimide. The alkyl bromide was employed for each of these preparations, unless otherwise indicated in the table.

It has been found that these imides lend themselves to the determination of saponification equivalents, since under mild conditions in the presence of a slight excess of dilute standard base the imide ring opens to form the salt of the related phthalamic acid. The saponification equivalent is determined



by titration of the excess standard base with hydrochloric acid, using *m*-cresol purple as indicator. Phenolphthalein was found to be unsatisfactory.

For characterization purposes, the combination of melting point and saponification equivalent will usually clearly distinguish two of the imides in Table I even though either alone might not suffice.

(2) O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1923, p. 164.

(3) P. P. T. Sah and T. S. Ma, *Ber.*, **65B**, 1630 (1932); *Science Repts. Natl. Tsing Hua Univ.*, **2**, 147 (1933).

(4) C. F. H. Allen and R. V. V. Nicholls, THIS JOURNAL, **56**, 1409 (1934).

(5) L. L. Merritt, S. Levey and H. B. Cutter, *ibid.*, **61**, 15 (1939).

TABLE I

N-ALKYL-4-NITROPHTHALIMIDES

N-Alkyl substituent	M.p.,[a] °C.	Yield,[b] %	Sapn. equiv. Calcd.	Sapn. equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl[c]	177–178	87.5[d]	206.1	205.0		
Ethyl[e]	114–115	80.6	220.2	218.3		
Propyl[e]	102–102.5	75.0	234.2	233.6		
Isopropyl	133–134	21.6[f]			11.94	11.98
Butyl[e]	95–96	82.5	248.3	245.4		
Isobutyl	127–128	46.7[f]	248.3	248.6	11.28	11.42
Amyl[e]	95–96	77.8	262.3	261.3		
Isoamyl	118–119	81.7	262.3	260.2	10.68	10.54
Hexyl[e]	94.5–95.5	74.3	276.3	275.1		
3-Methylpentyl	95.5–96	93.4	276.3	264.5	10.13	10.34
2-Ethylbutyl	88–89	66.8	276.3	276.0	10.13	10.17
Heptyl[e]	92–93	73.8	290.3	290.4		
Octyl[e]	88.5–89.5	87.4	304.3	303.9		
2-Ethylhexyl	61.5–62	80.7	304.3	306.1	9.21	9.20
Nonyl[e]	88–88.2[g]					
Decyl[e]	87.5–88.5	84.0	332.4	331.3		
Undecyl	86.5–87.5	23.6			8.09	8.10
Dodecyl	85.5–86	21.6			7.78	7.68
Tetradecyl	86.5–87	72.3			7.21	7.14
Hexadecyl	91.5–92	82.8	416.6	414.7	6.73	7.03
Octadecyl	91.5–92.5	96.6			6.30	6.55
Allyl	105.5–106.5	79.2[f]	232.2	231.3	12.06	12.26
Benzyl[e]	164–165	73.4[f]	282.2	282.5		
p-Nitrobenzyl	163–164	79.4[f]			12.83	12.85
2-Phenylethyl	144–144.5	58.4	296.3	296.2	9.47	9.33
3-Phenylpropyl	110.5–111.5	81.5[f]	310.3	307.3	9.04	8.82

[a] All melting points corrected. [b] Yield after recrystallization based on 4-nitrophthalimide or potassium 4-nitrophthalimide. [c] M. T. Bogert and R. R. Renshaw, THIS JOURNAL, **30**, 1135 (1908), found m.p. 179–180°. [d] Prepared from methyl iodide. [e] A. F. Kirkpatrick, Ph.D. Thesis, Penn State Coll., 1943, p. 17. [f] Prepared from the alkyl chloride. [g] Not prepared, m.p. value of Kirkpatrick.

It was found that N-benzyl-3-nitrophthalimide, prepared from benzylamine, also gave a satisfactory saponification equivalent by our procedure. This suggests that the N-alkyl-3-nitrophthalimides derived from other primary amines[6] would permit the determination of a saponification equivalent in the same manner.

Experimental

N-Alkyl-4-nitrophthalimides.—In a 250-ml. round-bottomed flask was placed either 2.4 g. (0.104 mole) of potassium 4-nitrophthalimide or preferably 2.0 g. (0.104 mole) of 4-nitrophthalimide and 0.9 g. (0.065 mole) of anhydrous potassium carbonate. If the alkyl halide was not an iodide, 0.2 g. of potassium iodide was also included. Then 2–3 ml. (2 g. if a solid) of the dry alkyl halide and 20 ml. of dimethylformamide[7] were added. Under a reflux condenser bearing a drying tube, the mixture was heated at 135–145° for 1.25 hours. With low-boiling halides the temperature was raised slowly to this range. The flask was shaken occasionally. Some color appeared in the mixture, and if potassium carbonate were a reactant, carbon dioxide was evolved.

The cooled reaction mixture was poured into 100 ml. of cold water, using another 50 ml. of water to wash out the flask. After collecting the solid, it was washed with successive 40-ml. portions of water, 2% sodium hydroxide solution,[8] and water again. The dried crude product was recrystallized by dissolving it in a slight excess of 95% ethanol, filtering while hot, concentrating the solution somewhat, and adding water dropwise until the turbidity just disappeared.

Determination of the Saponification Equivalent.—An approximately 0.6-g. sample of pure N-alkyl-4-nitrophthal-

(6) J. W. Alexander and S. M. McElvain, *ibid.*, **60**, 2285 (1938).

(7) Dimethylformamide requires care in handling. Breathing of the vapor or contact of the liquid with the skin is to be avoided.

(8) The brief washing with base to remove 4-nitrophthalimide may be omitted with little sacrifice of product purity. Prolonged contact with base causes loss of product by saponification.

imide was weighed exactly on a tared watch glass and washed into a 250-ml. erlenmeyer flask with 12 ml. of 95% ethanol. From a buret, 25.00 ml. of standard potassium hydroxide (about 0.2 *N*) was added and the corked flask was warmed at 50° until the solid completely dissolved. When it had cooled to room temperature, the solution was diluted to a volume of about 100 ml. and four drops of 0.05% *m*-cresol purple indicator was added. The excess base was then titrated with standard hydrochloric acid (about 0.12 *N*), taking as the end-point, the first definite yellow (no purple) tint. The saponification equivalent of the N-alkyl-4-nitrophthalimide was computed in the same manner as that of an ester.

Two compounds gave unsatisfactory results by this procedure. The N-octadecyl-4-nitrophthalimide forms a rather insoluble, soapy potassium salt and complete solution was not attained. In the case of the N-(*p*-nitrobenzyl)-4-nitrophthalimide, the basic solution containing the salt displayed a yellow-brown color rather than purple when the indicator was added.

N-Benzyl-3-nitrophthalimide.—This compound was prepared from benzylamine and 3-nitrophthalic anhydride by the procedure of Alexander and McElvain.[6] Its saponification equivalent was determined by the above procedure as 280.6 (calcd., 282.2).

CONTRIBUTION NO. 575, DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

Trifluoroacetyl Hypofluorite[1]

BY GEORGE H. CADY AND K. B. KELLOGG

RECEIVED NOVEMBER 11, 1952

For some time an investigation of the reactions of elementary fluorine with volatile carbon compounds containing oxygen has been under way in these laboratories. In the early stages of the work, the compound trifluoromethyl hypofluorite[2] was obtained by the fluorination of methanol or carbon monoxide. Later it was found that numerous organic compounds containing oxygen, such as ethanol, acetic acid, cyclohexanone, ethylene glycol and acetone, would react with fluorine, even by combustion, to produce trifluoromethyl hypofluorite as well as certain fluorinated hydrocarbons.

In another series of experiments fluorine was allowed to react at room temperature with various oxygen containing substances. In one case trifluoroacetic acid was placed in a platinum boat enclosed in a Teflon tube, and undiluted fluorine was passed over it. The reaction products which condensed in a trap cooled by liquid oxygen were found to be easily exploded by an electric spark. It was at once suspected that the explosive substance might be trifluoroacetyl hypofluorite formed by replacement of the hydrogen atom by fluorine. Attempts were then made to isolate and identify the compound. These efforts were discouraging. Sometimes no explosive product was obtained. At other times the substance exploded as the preparative reaction proceeded or while in the process of distillation. Several rather elaborate systems of glass apparatus were destroyed. Metallic systems were tried but the explosive compound was not obtained. Finally, the substance was prepared in a small amount as described below, and its molecular weight and composition were established.

The present article describes only exploratory experiments. There still remains a need for additional work in order that more properties of the substance may be known with precision.

Solutions believed to contain compounds of the formulas CF_3COOBr and CF_3COOI have been prepared by Henne and Zimmer[3] by the reaction of the free halogen with silver trifluoroacetate.

Materials.—Fluorine was used directly from cylinders obtained from the Pennsylvania Salt Manufacturing Co. Anhydrous trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Co. Usually it was used just as it came from the manufacturer; for some experiments, however, the acid was distilled. The distillation appeared to have little effect upon the reaction of the acid with fluorine.

Experimental.—Figure 1 shows the equipment finally used for the preparation and identification of the compound. Inlets for controlled and measured streams of fluorine and nitrogen were provided as shown at the left of the figure. Bubblers A and B contained water and trifluoroacetic acid held at 20 and 0°, respectively. Trifluoroacetic acid vapor and water vapor were swept by streams of nitrogen into vessels C and D, where the reaction with fluorine occurred. The part of the system between boundaries F and G was composed of polyethylene bottles and tubing, Saran tubing and rubber stoppers. A glass tube served as the inlet for fluorine into bottle C. Bottles C and D were kept at room temperature. They had a combined volume of 1060 ml. Bottle E was held at −78° and was used as a trap to condense hydrogen fluoride, water vapor and unreacted trifluoroacetic acid from the gas stream. From it the gas passed through the glass system and out through stopcock X. Among the products condensed in the trap, W, which was cooled to −183° by liquid oxygen, were: CF_3COOF, CF_4, COF_2, CO_2 and SiF_4. The remainder of the glass system was used for refining the product and for taking samples. Before use, the system was carefully cleaned and dried. Stopcocks were lubricated with a greasy wax composed of polymers of chlorotrifluoroethylene. This highly essential material was obtained from the M. W. Kellogg Co. of Jersey City, N. J., and from the Halocarbon Products Corp. of North Bergen, N. J.

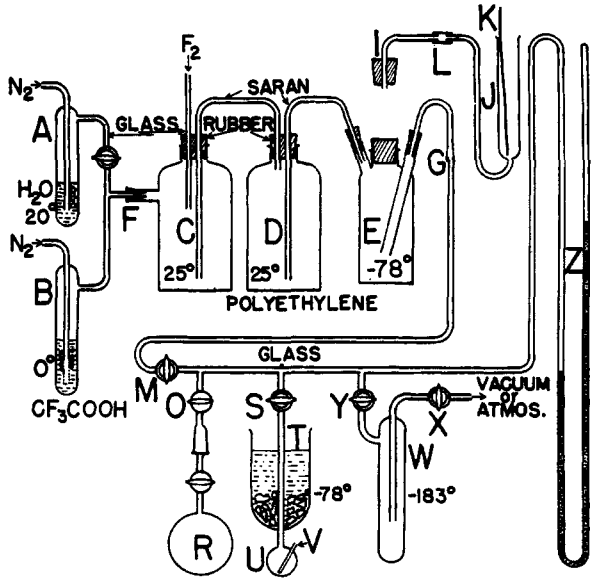


FIG. 1.

(1) This compound was mentioned in an article about the industrial production of fluorine chemicals at the Minnesota Mining and Manufacturing Co. [*Chem. Eng. News*, **29**, 4488 (1951)]. A letter to one of the authors from N. W. Taylor, Manager of the Fluorochemicals Department of that company states, "The story in Chemical and Engineering News referring to this type of product was due to a misunderstanding on the part of the editor. . . As far as 3M is concerned, you are the inventor of CF_3COOF."

(2) K. B. Kellogg and George H. Cady, THIS JOURNAL, **70**, 3986 (1948).

(3) A. L. Henne and W. F. Zimmer, *ibid.*, **73**, 1362 (1951).