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	$i\text{-}C_3H_7I$	$n\text{-}C_3H_7I$	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.

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A New Synthesis of Aminomalonic Acid[1]

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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.

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[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).

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

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RECEIVED NOVEMBER 8, 1952

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

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