trated solution of II in chloroform; instances of bromination of isomeric diacetoxyacetophenones are reported by Mosimann and Tambor[14] and by Shriner and Witte.[15] Thus 0.41 g. (2.57 mM.) of bromine was passed into a solution of 0.605 g. (2.57 mM.) of recrystallized II in 3.5 ml. of chloroform (reagent grade, 0.75% ethanol) at room temperature under anhydrous conditions. The velocity of the nitrogen stream was controlled in such a way that no appreciable amounts of free bromine emerged from the solution. When, at the start of the reaction, the solution had become colored with bromine, the nitrogen stream was interrupted and the mixture was allowed to decolorize before proceeding; reaction with bromine occurred rapidly after this induction period. After all the bromine had been consumed (an hour was usually required), the nitrogen stream was quickened to sweep out hydrogen bromide and most of the solvent, solvent removal being facilitated by warming the reaction vessel finally to about 40°. On completion of evaporation *in vacuo*, the crude product solidified. Recrystallization from isopropyl ether–ethanol gave pure III, clusters of colorless needles, m.p. 96–98°, weighing 0.575 g. (71.1%; yields in other runs varied only from 70 to 72%). Mother liquors yielded no further amounts of III. The analytical sample, after repeated recrystallization, melted at 99.2–99.8°.

Anal. Calcd. for $C_{12}H_{11}BrO_5$: C, 45.73; H, 3.52; Br, 25.36. Found: C, 45.67; H, 3.55; Br, 25.30.

3,4-Diacetoxy-α-phthalimidoacetophenone (IV).—Conversion of an α-haloacetoxyacetophenone to an α-aminohydroxyacetophenone *via* the α-phthalimido ketone has been described by Tutin, *et al.*[16] A mixture of 0.575 g. (1.827 mM.) of recrystallized III, 0.37 g. (10% excess) of potassium pthalimide and 1 ml. of dimethylformamide[17] (freed of traces of moisture by azeotropic distillation with benzene) was heated in steam for about one minute, cooled in ice, and the product partitioned between chloroform and water. Washed with 0.2 *N* sodium hydroxide, dried ($MgSO_4$), and freed of solvent, the chloroform extracts gave crude solid IV (0.655 g.). Recrystallization from ethanol–ethyl acetate yielded 0.36 g. (43.1%) of pure IV, clustered colorless slabs, m.p. 156–157°. A sample of IV obtained in another experiment melted slightly higher, at 156.8–157.8°. Yields of pure IV (based on III) in other experiments were as high as 58%; model experiments on phenacyl bromide gave comparable yields of α-phthalimidoacetophenone, in contrast to the near-quantitative yields reported.[17]

Anal. Calcd. for $C_{20}H_{15}NO_7$: C, 62.99; H, 3.97; N, 3.67. Found: C, 62.83; H, 4.04; N, 3.61.

***dl*-α-(Aminomethyl)-3,4-dihydroxybenzyl Alcohol (*dl*-Arterenol) Hydrochloride (VI).**—IV (0.64 g.) was hydrolyzed by heating with a mixture of 1.5 ml. each of 12 *N* HCl and glacial acetic acid sealed in a nitrogen-filled tube at 100° for seven days. The contents of the tube then were diluted with distilled water to 25 ml., filtered from a small amount of phthalic acid, and hydrogenated over 10% Pd-on-charcoal (American Platinum Works) at 25° and at atmospheric pressure. A total of 48 ml. of moist hydrogen was absorbed (theory 43 ml.). Filtered free of catalyst, extracted with ether to remove residual traces of phthalic acid and evaporated to dryness from the frozen state, the mixture gave the theoretical yield (0.32 g.) of crystalline, near-colorless VI. For analysis, a sample of the salt was precipitated from an absolute ethanol solution by addition of anhydrous ether.

Anal. Calcd. for $C_8H_{12}ClNO_3$: C, 46.72; H, 5.88; Cl, 17.24; N, 6.81. Found: C, 46.61; H, 6.00; Cl, 17.20; N, 6.77.

The ultraviolet absorption spectrum of VI dissolved in 0.1 *N* HCl corresponded closely with another of authentic *dl*-arterenol hydrochloride, showing a maximum at 279 and a minimum at 252 mμ.

Radioactivity of the sample of α-C^{14}-VI was determined (by conventional methods) to be 16 mc./mM. (calcd. from $BaC^{14}O_3$ 17.6). Biological activity of the radioactive substance was determined using a pithed male cat. The carotid artery was cannulated for recording arterial pressure changes *via* the Statham pressure transducer and an Offner oscillograph. A three-point standard curve of authentic VI was obtained by injecting increasing amounts of the substance up to but not including decreased linearity of response; the presence of 70 ± 14 mg. of VI in a solution containing 55 mg. of the synthetic radioactive material was thus indicated.

Dilute solutions of C^{14}-VI undergo appreciable deterioration even when stored under mild conditions. Thus after several months' storage at 0° of a solution of 55 mg. of the substance in 50 ml. of 0.001 *N* HCl, 0.001 *N* $NaHSO_3$ under nitrogen, its ultraviolet spectrum was noted to have changed; the change was manifest principally by a decrease in the absorptivity ratio ($a_{max}:a_{min}$), presumably as a consequence of increased end absorption attributed to decomposition products. Paper chromatography of the altered solution indicated the presence of several labeled contaminants, two (about 10 and 20% of the total counts) with R_f's smaller and one (about 5%) with an R_f greater than that of VI.[18]

A chromatographically pure sample of C^{14}-VI was obtained by placing a sample of the storage-deteriorated solution on Whatman No. 1 paper presprayed with ascorbic acid (50 mg./100 ml.) and developing with phenol (85 g.)–0.1 *N* HCl (15 ml.) in an SO_2 atmosphere. After removing the phenol by washing the paper with benzene, it was dried at room temperature and the C^{14}-VI area cut out and extracted with 0.2 *N* formic acid (recovery > 90%). Rechromatography showed no persistent contamination.

(14) W. Mosimann and J. Tambor, *Ber.*, **49**, 1263 (1916).

(15) R. L. Shriner and M. Witte, THIS JOURNAL, **61**, 2328 (1939).

(16) F. Tutin, F. W. Caton and A. C. O. Hann, *J. Chem. Soc.*, **95**, 2113 (1909).

(17) J. C. Sheehan and W. A. Bolhofer, THIS JOURNAL, **72**, 2786 (1950).

(18) The possibility is not excluded that some of these contaminating substances are present in the freshly-prepared product; thus one (tentatively identified by its R_f) appeared to be dopamine β-(3,4-dihydroxyphenyl)-ethylamine, which might well have been produced by hydrogenolysis of VI. The authors are indebted to Dr. David Masuoka for these chromatographic studies.

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Reactions of Haloketones, Allylic Chlorides and N-Chlorosuccinimide with Ketene Acetal. Orthoester Reactions *via* Chloroacetone[1]

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RECEIVED NOVEMBER 17, 1954

The reactions of many organic halides with ketene acetal have been reviewed by McElvain.[3] We have studied the reactions of a number of halides of diverse type with this substance and are reporting our results here.

The action of chloroacetone and of bromoacetone on ketene acetal leads mainly to polymerization of the latter, although small amounts of ethyl levulinate are formed, as are ethyl acetate, ethyl orthoacetate and ethanol, known decomposition products of ketene acetal. Ethyl orthoacetate at 110° with chloroacetone likewise gives ethyl levulinate and normal decomposition products of ketene acetal. It is possible that ketene acetal is an intermediate in this reaction. Since the action of chloroacetone on ketene acetal leads to isolation of ketene acetal dimer (16%) and trimers (15%), this polymerization is similar in effect to that brought about by hydrogen fluoride.[4,5]

(1) Abstracted in part from the Ph.D. thesis of Eugene E. Richardson submitted to the Graduate Faculty of Kansas State College, Manhattan, as partial fulfillment for the Degree, Doctor of Philosophy in Chemistry.

(2) Research Corporation Research Assistant.

(3) S. M. McElvain, *Chem. Revs.*, **45**, 453 (1949).

(4) S. M. McElvain and D. Kundiger, THIS JOURNAL, **64**, 254 (1942).

(5) S. M. McElvain and J. W. Langston, *ibid.*, **65**, 2289 (1943).

While chloroacetone gives no indication of condensing with itself, bromoacetone forms a self-condensation product having the same constitution whether formed in the presence of ketene acetal or in its absence, and for which we have not been able to formulate a reasonable structure. This self-condensation product of bromoacetone has not been reported previously, although Brendler[6] obtained indirect indications of it.

The relative reactivities of the allylic chlorides I and II with ketene acetal also were determined. II should be more reactive on the basis of inductive effects. On heating for four hours at 190–200° with ketene acetal, I gave ethyl 3,3-dichloro-2-

$Cl_2C{=}C(CH_3)CH_2Cl$ (I) $CH_2{=}CHCH_2Cl$ (II)

methylallylacetate (III) in 21% yield, whereas II gave ethyl allylacetate in 35% yield. Also produced in these reactions was an unsaturated gas, presumably ethylene, in yields of 69 and 95% from the available ketene acetal. Since pyrolysis of the latter at 200° does not normally yield more than 20% of ethylene,[7] these chlorides appear to function as catalysts for the decomposition of ketene acetal.

N-Chlorosuccinimide reacts with ketene acetal to form ethyl chloroacetate in 44% yield, succinimide in 90% yield and an unsaturated gas, presumably ethylene. Since no ethyl chloride is formed and since also no product can be detected corresponding to addition of succinimidyl free radical to the anionoid methylene carbon of ketene acetal, it appears that succinimidate anion is indicated as the main reactive species.

Acknowledgment.—We acknowledge with thanks our indebtedness to the Research Corporation which supported this research.

Experimental Part[8]

Ketene acetal (K. A.) was prepared by a modification[9] in which the barostat system formerly used was dispensed with, and all distillations were performed at atmospheric pressure with an electrical heating mantle over the whole of the still-pot. 1,1,3-Trichloro-2-methyl-1-propene (Allyl TMP) was prepared by the method of Kundiger and Haney.[10]

Chloroacetone and bromoacetone (the Matheson Co.) were purified by standing over calcium carbonate (no reaction), distillation under low vacuum and storage over calcium carbonate (no reaction).

Reactions of Chloroacetone with K. A.—A mixture of 69.7 g. (0.75 mole) of chloroacetone and 87.0 g. (0.75 mole) of ketene acetal was refluxed for 24 hours under anhydrous conditions. At the end of this time, 4.0 g. (8%) of ethyl chloride, b.p. 12–13°, had collected in the Dry Ice trap. Fractionation of the reaction mixture, followed in most cases by redistillation of individual fractions, gave 17.3 g. of a mixture of ethanol and ethyl acetate, b.p. 75–83°, 62.6 g. (90%) of recovered chloroacetone, b.p. 115–119°; 2.5 g. (2%) of ethyl orthoacetate, b.p. 144–148°; 14.1 g. (16%) of ketene acetal dimer, b.p. 58–61° (0.5 mm.) (reported[11] 61–62° (0.5 mm.)), characterized by conversion[11] to the semicarbazone of ethyl acetoacetate, m.p. 128.7–129.5°[12]; 6.0 g. of crude ethyl levulinate, b.p. 86–88° (1 mm.), which was purified by low-temperature crystallization to give 4.0 g. (46.7% based on chloroacetone consumed) of pure ethyl levulinate, b.p. 204–206°, 2,4-dinitrophenylhydrazone, m.p. 99.2–100.5°, oxime 35.8–36.5°; and finally, 13.0 g. (15%) of crude ketene acetal trimer, b.p. 130–142° (0.5 mm.), which had 74.1% ethoxyl (acceptable and in agreement with the reported value[11]).

Reaction of Ethyl Orthoacetate with Chloroacetone in Presence of Phenol.—A mixture of 41.5 g. (0.5 mole) of chloroacetone and 42.0 g. (0.47 mole) of phenol was heated and stirred at 110° while 81.0 g. (0.5 mole) of ethyl orthoacetate was added dropwise; the reaction was allowed to proceed for 18 hours. Fractionation of the reaction mixture, followed in most cases by redistillation of individual fractions, gave 49.2 g. of a mixture of ethyl acetate and ethanol, b.p. 72–78°; 23.9 g. (58%) chloroacetone, b.p. 114–121°; 28.7 g. of a mixture of phenol and phenetole, b.p. 91–105° (18 mm.); 22.8 g. of a mixture of mostly phenyl acetate and a little diethyl phenyl orthoacetate, b.p. 71–75° (2.5 mm.); 14.2 g. of ethyl levulinate, b.p. 89–100° (2.5–3.5 mm.); and 18.9 g. of polymerized tarry material. The ethyl levulinate redistilled at b.p. 202–206°, yield 18%, 2,4-dinitrophenylhydrazone, m.p. 101–102°, no depression of mixed m.p. with an authentic sample. The mixture of phenol and phenetole was extracted with 5% sodium hydroxide, with water and with ether. Drying of the ether extract followed by distillation gave 16.6 g. of phenetole, b.p. 171–173°, which was cleaved to phenol, m.p. 42.5–43.6°, and to ethyl iodide, b.p. 72–73.4°. From the alkaline extract, phenol (12.1 g.) was obtained.

The mixture, consisting mostly of phenyl acetate and a little diethyl phenyl orthoacetate,[4] was characterized by pyrolysis, *i.e.*, refluxing 20 minutes through a heated packed column,[4] followed by distillation. The diethyl phenyl orthoacetate decomposed to ethyl acetate, b.p. 75–80°; 4.1 g. of phenetole, b.p. 170–174°; and 10.4 g. (15% based on ethyl orthoacetate) of phenyl acetate, b.p. 193–195°. Total yield of phenetole was 20.7 g. (34%). The phenyl acetate was identified by conversion to phenol, m.p. 42.2–43.5°, and acetic acid (*p*-phenylphenacyl ester, m.p. 110–111°).

When a small amount of ethyl orthoacetate (11.0 g., 0.068 mole) was treated with 69.7 (0.75 mole) of the purified chloroacetone at 119° for 24 hours, there was 1.1 g. of ethyl chloride, b.p. 12–13°, in the Dry Ice trap. Fractionation of the reaction mixture gave 6.1 g. of a mixture of ethyl acetate and ethanol, b.p. 75–80°, also 67.0 g. of chloroacetone, b.p. 115–119° and 4.0 g. of tar.

Reactions of Bromoacetone with K. A.—To 54.8 g. of bromoacetone maintained at 30–40° by cooling, 35 g. (0.32 mole) of K. A. was added dropwise (0.75 hour) with stirring. The reaction was exothermic. It was found necessary to hold the reaction temperature below about 40° in order to avoid excessive tar. After further reaction (1 hour), 62.2 g. of material was recovered under water-pump and oil-pump vacuum and collected in Dry Ice traps. Fractionation of this material gave 4.8 g. of ethyl bromide, b.p. 37–46°; 18.5 g. of ethyl acetate, b.p. 72–78°; 13.9 g. of bromoacetone, b.p. 41–43° (17 mm.); 6.2 g. (11.3%) of the self-condensation product of bromoacetone, b.p. 59–61° (2.5 mm.), accompanied by 7.8 g. of Dry Ice trap liquid and 9.1 g. of residual liquid, which solidified and was extracted repeatedly with acetone. Evaporation of the acetone extract gave a reddish-brown material, which, upon recrystallization from absolute ethanol gave 2.7 g. of colorless K. A. cyclic trimer (1,1,3,3,5,5-hexaethoxycyclohexane), m.p. 68–73° (reported 72–73°[5,11]).

The residue that remained after removal of the above 62.2 g. of material, was distilled. Of the 15.1 g. of distillate, a 6.4-g. portion was fractionated and gave 3.5 g. of ethyl levulinate, b.p. 98–101° (3.5 mm.); 31.7% ethoxyl (calcd. 31.3%), 2,4-dinitrophenylhydrazone, m.p. 100.5–101.7°, and oxime, m.p. 37–38°.

The self-condensation product of bromoacetone had 42.5% bromine, showed no unsaturation toward bromine, formed a solid product with 2,4-dinitrophenylhydrazine that could not be crystallized. The original distillate was colorless but turned purple upon exposure to air and later became tarry.

Self-condensation Product of Bromoacetone.—Water-white bromoacetone that was stored in the presence of air for several months became purple. This bromoacetone (50 g.) was heated under anhydrous conditions at 45° for 1.75

(6) W. Brendler and J. Tofel, *Ber.*, **31**, 2683 (1898).

(7) S. M. McElvain, H. I. Anthes and S. H. Shapiro, THIS JOURNAL, **64**, 2525 (1942).

(8) All m.p.'s and b.p.'s are uncorrected.

(9) S. M. McElvain and D. G. Kundiger, *Org. Syntheses*, **23**, 45 (1943).

(10) D. G. Kundiger and H. N. Haney, THIS JOURNAL, **76**, 615 (1954).

(11) P. R. Johnson, H. M. Barnes and S. M. McElvain, *ibid.*, **62**, 964 (1940).

(12) J. Thiele and O. Stange, *Ann.*, **283**, 29 (1894).

hours. Immediate fractionation at 2.5 mm. gave 30.1 g. of bromoacetone in the Dry Ice trap and 6.3 g. (12%) of the self-condensation product, b.p. 56–60° (2.5 mm.), 42% bromine (42.5% when K. A. was present as per the above). The other properties of this product were the same as in the case of the former sample prepared as above.

Reactions of K. A. with 1,1,3-Trichloro-2-methyl-1-propene (I).—A mixture of 27.0 g. (0.234 mole) of K. A. and 38.6 g. (0.24 mole) of I was heated in sealed, necessarily new rigorously dried[7] Pyrex bomb tubes held at 190–200° for 4 hours. The tubes contained a high pressure of ethylene. There were isolated as products: 2.1 g. (21%) of ethyl chloride, b.p. 12–12.5°; 17.6 g. of ethyl acetate with about 4% of ethanol present, b.p. 70–80°, 13.7 g. of recovered I, mostly taken at b.p. 36–38° (0.8 mm.); 4.5 g. of ethyl 3,3-dichloro-2-methylallylacetate (III), b.p. 67–73° (1.1 mm.), of which an analytically pure cut had b.p. 66–68° (0.4 mm.), sapn. equiv. 216 (calcd. 211), 33.81% Cl (calcd. 33.79% Cl), 20.8% ethoxy (calcd. 21.38%).

K. A. with Allyl Chloride (II).—A mixture of 0.157-mole amounts of these substances was heated and handled as above for I. After venting the ethylene, fractionation of the reaction mixture gave 1.03 g. (22%) of ethyl chloride, b.p. 12–12.5°; 6.5 g. of allyl chloride, b.p. 43–45°; 8.0 g. of 95% ethyl acetate and 5% ethanol, b.p. 70–79°; and 3.2 g. (35.2%) of ethyl allylacetate, b.p. 78–80° (80 mm.), sapn. equiv. 129.3 (calcd. 128.0). 35.4% ethoxyl (calcd. 35.2%), and b.p. 140–142°.[13]

Reaction of N-Chlorosuccinimide with K. A.—A solution of 32.1 g. (0.241 mole) of N-chlorosuccinimide in 190 ml. of absolute carbon tetrachloride was refluxed at 76–77° while K. A. (28.0 g., 0.241 mole) was added dropwise (two hours). Ethylene was evolved with extreme frothing. It was identified by reaction with permanganate and with bromine in carbon tetrachloride; no ethyl chloride could be detected. After further reaction at 76° for 2.5 hours and at 35° for 12 hours, the reaction mixture was concentrated with occasional removal of the precipitated succinimide. A total of 21.0 g. (90.1%), m.p. 123–124°, was collected. Fractionation of the remaining liquid gave 15.2 g. of a mixture of products, b.p. 39–41° (0.25 mm.). Fractionation of a 10.1-g. portion of this gave 5.7 g. (29%) of analytically pure ethyl chloroacetate, b.p. 145–146°, 27.9% Cl (calcd. 28.01%), and 36.5% ethoxyl (calcd. 36.8%). It was converted to phenoxyacetic acid, m.p. 97.9–98.7°, no depression on admixture with known phenoxyacetic acid. From another experiment, 18.1 g. of distillate, b.p. 70–72° (5.0 mm.) was obtained after removal of succinimide. Redistillation of this distillate gave 13.2 g. (44%) of ethyl chloroacetate, b.p. 144–147°.

(13) F. Zeidler, *Ann.*, **187**, 39 (1877).

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A Simplified Procedure for the Synthesis of 2,4-Dinitrophenyl(DNP)-amino Acids

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RECEIVED DECEMBER 10, 1954

The original method employed by Sanger[3] for the synthesis of DNP amino acids has been unmodified by later workers in the field of end group and amino acid analysis. The procedure comprises shaking the amino acid with a twofold excess of 1-fluoro-2,4-dinitrobenzene (FDNB) and an equal weight of sodium bicarbonate in 67% ethanol (by volume) for two hours at room temperature, followed by evaporation of the ethanol, dilution with water, and extraction of excess FDNB with ether. Acidification then yields the required DNP amino acid.

(1) Deceased, August 21, 1954.

(2) This manuscript was revised from the notes of the late Dr. Levy.—C. H. Li.

(3) F. Sanger, *Biochem. J.*, **39**, 507 (1945).

It has been found that several advantages result from working in an aqueous solution at a somewhat higher *p*H (9.0) and a slightly elevated temperature (40°) and from employing only an equivalent amount of FDNB: a more rapid reaction can be achieved, ethanol evaporation and extraction of excess FDNB can be eliminated and a purer product results with greater economy of reagents. By means of this simplified procedure,[4] we have prepared in crystalline form DNP derivatives of the known amino acids, including DNP-L-glutamic acid and bis-DNP-L-cysteine. The syntheses of these latter two derivatives have not been reported hitherto. Crystalline DNP-DL-methionine sulfoxide, DNP-DL-methionine sulfone and DNP-DL-alanylglycylglycine also have been prepared.

The time needed for reaction varies for different amino acids but rarely exceeds 1 hour (at 40°), except in the case of complete substitution of the imidazole group of histidine, which requires a considerably longer time, so that more than two equivalents of FDNB are needed. In general, DNP-DL-amino acids crystallized more readily than the corresponding L-derivatives, particularly in the cases of glutamic acid, methionine, leucine and tyrosine.

Experimental[5]

DNP-L-leucine.[5]—L-Leucine (Schwarz Laboratories, Inc., Mt. Vernon, N. Y., 1.30 g.) and sodium carbonate (anhydrous, 2.0 g.) were dissolved in 40 ml. of water at 40°. FDNB (Eastman Kodak Co., 1.85 g.) was introduced, and the mixture was stirred vigorously by means of a magnetic stirrer, the temperature being maintained at about 40°. The finely divided suspension of FDNB disappeared after about 30 minutes indicating that the reaction was complete. Acidification (concentrated hydrochloric acid, 3 ml.) of the resulting orange solution yielded DNP-L-leucine, which crystallized on rubbing (yield 2.89 g., 97%, the remaining 3% appearing as dinitrophenol). It was recrystallized from carbon tetrachloride and subsequently from aqueous acetic acid, as yellow needles, m.p. 101° (uncor.) and $[\alpha]^{23}D$ +56.6° (1% $NaHCO_3$).

Anal. Calcd. for $C_{12}H_{15}O_6N_3$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.50; H, 4.99; N, 13.98.

It is perhaps worth mentioning that L-leucine from another commercial source yielded crystals only with great difficulty; synthetic L-leucine, however, readily afforded a crystalline DNP derivative.

DNP-L-Glutamic Acid.—By the method described above, 2.9 g. of L-glutamic acid, 3.7 g. of DNFB and 6.0 g. of Na_2CO_3 yielded 5.08 g. (81%) of the product after recrystallization from ethyl acetate–chloroform; m.p. 134–136°, $[\alpha]^{23}D$ −18.48° (1% $NaHCO_3$).

Anal. Calcd. for $C_{11}H_{11}N_3O_8$: C, 42.17; H, 3.51; N, 13.42. Found: C, 42.07; H, 3.66; N, 13.25.

DNP-DL-Methionine Sulfoxide.—By the same procedure 1.65 g. of DL-methionine sulfoxide, 1.85 g. of DNFB and 2 g. of Na_2CO_3 yielded 3.18 g. (96%) of the product, recrystallized from hot ethanol; m.p. 184.5° dec.

(4) Greater control can be effected by carrying out the reaction at *p*H 9.0 (glass electrode), and adding 2 *N* sodium hydroxide intermittently to maintain the *p*H at this value. The rate of addition of alkali then serves to indicate the rate of the reactions and results in the consumption of the theoretical 2 equivalents per amino group, provided that the alkali needed to titrate the amino acid from isoelectric condition to *p*H 9.0 is included.

(5) Since this manuscript was prepared for publication, Rao and Sober (THIS JOURNAL, **76**, 1328 (1954)) reported the preparation of DNP-L-leucine by the procedure of Sanger and gave its m.p. as 94–95° (uncor.) and $[\alpha]^{24}D$ +59.25° (4% $NaHCO_3$). The following description of its synthesis in crystalline form serves as an illustration of the method.