[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS]

New Methods of Introducing the Carbo-*t*-butoxy Protective Group. Preparation of *t*-Butyl Cyanoformate[1]

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A convenient synthesis of *t*-butyl carbazate from *t*-butyl S-methyl thiolcarbonate is described. A new carbo-*t*-butoxylating agent, *t*-butyl cyanoformate, has been prepared. Aminolysis of ethyl *t*-butyl oxalate yields *t*-butyl oxamate which is dehydrated by means of trifluoroacetic anhydride and pyridine to the cyanoformate. A novel conversion of dihydroxamic acids to the corresponding carboxylic anhydrides by means of nitrous acid is presented.

Following a description of its use as a protective group on nitrogen[2] the carbo-*t*-butoxy group has been shown to possess a number of advantages over other blocking functions,[3-5] particularly in the synthesis of sensitive nitrogen compounds.[6a,b] Because of the instability of *t*-butyl chloroformate[7] it has been necessary to develop special procedures for the introduction of the carbo-*t*-butoxy group. The reaction of an isocyanate with *t*-butyl alcohol is inconvenient for most derivatives.[8] *t*-Butyl phenyl[2,5] and *p*-nitrophenyl[4] carbonates have been used as acylating agents with success, particularly the latter. Although it is somewhat sluggish in its reaction with weakly basic amines, *t*-butyl azidoformate[3,6a,b] has been shown to be a carbo-*t*-butoxylating agent of fairly general applicability.

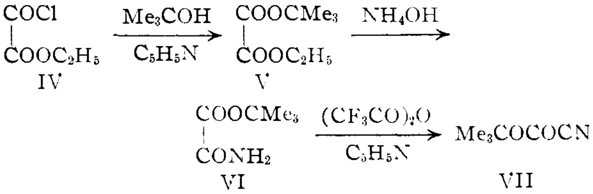
The present paper is concerned with a study of new routes to *t*-butyl carbazate (III), a key intermediate in the synthesis of *t*-butyl azidoformate, and with an investigation of synthetic routes to two other possible acylating agents, *t*-butyl cyanoformate and *t*-butyl carbonic anhydride. The earlier described method[2] for the preparation of *t*-butyl carbazate, while easily carried out on a large scale, affords a product which is difficult to free from traces of phenol. A new method now has been developed by which the carbazate may be obtained easily in a state of high purity. Sodium *t*-butoxide was treated with carbonyl sulfide and the resultant salt methylated to give *t*-butyl S-methyl thiolcarbonate which with hydrazine hydrate at 105–110° gave pure III.

$$\mathrm{Me_3CONa} \xrightarrow{\mathrm{COS}} \underset{\mathrm{I}}{\mathrm{Me_3COCOSNa}} \xrightarrow{\mathrm{MeI}} \underset{\mathrm{II}}{\mathrm{Me_3COCOSMe}}$$

$$\xrightarrow{\mathrm{NH_2NH_2}} \underset{\mathrm{III}}{\mathrm{NH_2NHCOOCMe_3}}$$

Other potential carbazate syntheses examined included reaction of hydrazine with (a) *t*-butyl trichloroacetate,[9] (b) *t*-butyl α-nitroisobutyrate[10] and (c) *t*-butyl ethyl carbonate. The first two esters afforded low (30–40%) yields of the carbazate.

Alkyl cyanoformates[11] are most often prepared in quantity from alkyl chloroformates.[12] Methods which might be capable of application in the *t*-butyl series involve the dehydration[13,14] of the corresponding amide, *t*-butyl oxamate (VI) or oxime, *t*-butyl oximinoacetate. *t*-Butyl oxamate could be obtained only in trace amounts by reaction of *t*-butyl oxalate[15] with aqueous or alcoholic ammonia. On the other hand, the mixed ester *t*-butyl ethyl oxalate (V) proved to be a convenient intermediate in the synthesis of VI. Conversion of the oxamate VI to *t*-butyl cyanoformate (VII) proved to be difficult. None of the usual methods such as those involving phosphorus pentoxide,[16] phosphorus pentoxide–triethylamine,[17] *p*-toluenesulfonyl chloride–pyridine,[18] phosphorus trichloride,[19] phosphorus oxychloride[20] or thionyl chloride[21] was successful, although several of these methods were shown to work well in the case of the corresponding *n*-butyl derivative. Finally a smooth conversion of VI to VII was achieved by treatment



$$\underset{\mathrm{IV}}{\begin{array}{l}\mathrm{COCl}\\ |\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{Me_3COH}} \underset{\mathrm{V}}{\begin{array}{l}\mathrm{COOCMe_3}\\ |\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{NH_4OH}}$$

$$\underset{\mathrm{VI}}{\begin{array}{l}\mathrm{COOCMe_3}\\ |\\ \mathrm{CONH_2}\end{array}} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{(CF_3CO)_2O}} \underset{\mathrm{VII}}{\mathrm{Me_3COCOCN}}$$

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(1) Supported by a grant (NSF G2368) from the National Science Foundation.

(2) L. A. Carpino, THIS JOURNAL, **79**, 98 (1957).

(3) L. A. Carpino, *ibid.*, **79**, 4427 (1957).

(4) G. W. Anderson and A. C. McGregor, *ibid.*, **79**, 6180 (1957).

(5) F. C. McKay and N. F. Albertson, *ibid.*, **79**, 4686 (1957).

(6) (a) L. A. Carpino, C. A. Giza and B. A. Carpino, *ibid.*, **81**, 955 (1959); (b) L. A. Carpino, P. J. Crowley and P. H. Terry, manuscript in preparation.

(7) A. R. Choppin and J. W. Rogers, *ibid.*, **70**, 2967 (1948).

(8) *t*-Butyl carbamate may be prepared by a novel method which utilizes β-bromopropionyl isocyanate, the readily available free radical rearrangement product of N-bromosuccinimide [H. W. Johnson and D. E. Bublitz, *ibid.*, **80**, 3150 (1958)]. Reaction of the isocyanate with *t*-butyl alcohol gave *t*-butyl N-β-bromopropionylcarbamate from which the β-bromopropionyl group could be removed by selective alkaline hydrolysis.

(9) Ethyl trichloroacetate has been shown to react with primary and secondary amines with the formation of the corresponding amides and carbamates, respectively [M. M. Joullié and A. R. Day, *ibid.*, **76**, 2990 (1954)].

(10) With a dinitro ester such as ethyl α,α-dinitropropionate cleavage with hydrazine takes place readily at room temperature [L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **23**, 1340 (1958)].

(11) The acylating properties of alkyl cyanoformates have been described previously; see A. Weddige, *J. prakt. Chem.*, [2] **10**, 193 (1874).

(12) J. U. Nef, *Ann.*, **287**, 265 (1895).

(13) E. Ott, *Ber.*, **52**, 656 (1919).

(14) L. Bouveault and A. Wahl, *Bull. soc. chim. France*, [3] **31**, 675 (1904).

(15) H. J. Backer and J. D. H. Homan, *Rec. trav. chim.*, **58**, 1048 (1939).

(16) W. E. Bachmann and C. H. Boatner, THIS JOURNAL, **58**, 2097 (1936).

(17) S. M. McElvain and R. L. Clarke, *ibid.*, **69**, 2657 (1947).

(18) C. R. Stephens, E. J. Bianco and F. J. Pilgrim, *ibid.*, **77**, 1701 (1955).

(19) F. Salmon-Legagneur, *Bull. soc. chim. France*, 580 (1952).

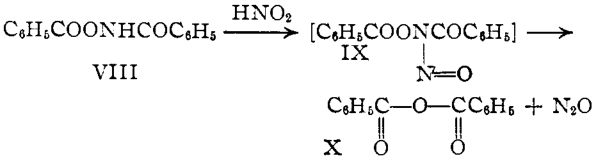
(20) W. B. Reid and J. H. Hunter, THIS JOURNAL, **70**, 3515 (1948).

(21) S. M. McElvain and C. L. Stevens, *ibid.*, **69**, 2663 (1947).

of VI with trifluoroacetic anhydride and pyridine. As an acylating agent, *t*-butyl cyanoformate proved to be more reactive than the corresponding azide although the crude reaction products obtained from the cyanide were often contaminated by dark-colored impurities.

Although attempts to obtain *t*-butylcarbonic anhydride (XII) were not successful, the reaction employed is of interest as a novel method of converting O,N-diacylhydroxylamines to the corresponding carboxylic anhydrides.

It has been shown that N-nitroso-N-alkyl amides, upon pyrolysis, yield the corresponding esters with expulsion of nitrogen.[22] Treatment of O-alkylhydroxylamines,[23] hydroxamic acids[24] and benzylhydroxamidic acids[25] with nitrous acid yields nitrous oxide in each case and alcohols, carboxylic acids and benzamides, respectively, as the organic products. The N-nitroso derivative IX of dibenzhydroxamic acid (VIII) might be expected to yield benzoic anhydride by loss of nitrous oxide. Treatment of VIII with the nitrous fumes derived from reaction of sodium nitrite with nitric acid gave benzoic anhydride (X) directly in 88.5% yield. An intermediate nitroso compound such as IX was not observed. Unfortunately, application of this reaction to *t*-butyl N-*t*-butyloxycarbonyloxycarbamate[6a] (XI) was not successful, possibly because of decomposition of the expected anhydride XII.



$$\underset{\text{VIII}}{C_6H_5COONHCOC_6H_5} \xrightarrow{HNO_2} \underset{\text{IX}}{[C_6H_5COO\underset{\underset{N=O}{|}}{N}COC_6H_5]} \longrightarrow \underset{\text{X}}{C_6H_5\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}C_6H_5} + N_2O$$

$$\underset{\text{XI}}{Me_3COCOONHCOOCMe_3} \qquad \underset{\text{XII}}{(Me_3COCO)_2O}$$

Experimental[26-28]

***t*-Butyl S-Methyl Thiolcarbonate.**—A slurry of sodium *t*-butoxide was prepared by refluxing a mechanically-stirred mixture of 46 g. of sodium and 1500 ml. of *t*-butyl alcohol for 24–30 hours. The source of heat was removed and a stream of carbon oxysulfide (The Matheson Co.) was passed into the resulting well-stirred mixture until spontaneous refluxing ceased and the temperature began to drop (about 2 hours). The mixture was treated with 355 g. of methyl iodide over a 15–20-minute period (spontaneous warming occurred) and allowed to stir overnight at room temperature. The inorganic salts were dissolved by the addition of 1 l. of water which caused phase separation. The upper organic layer was separated and the lower layer was extracted with four 40-ml. portions of ether. The combined organic layers were dried by the addition of solid potassium carbonate until the newly formed aqueous layer did not increase in amount. The layers were separated and the upper layer treated with potassium carbonate a second time. The ether and *t*-butyl alcohol were removed by distillation through a column at atmospheric pressure until the volume reached about 400 ml. The distillation was continued with the aid of a water aspirator. After removal of the residual alcohol the ester was collected as a yellowish liquid, b.p. 60–62° (20 mm.), amount 192.5 g. (65%). The analytical sample was prepared by distillation at atmospheric pressure, b.p. 145°, λ_{max} 5.90 μ (C=O).

Anal. Calcd. for $C_6H_{12}O_2S$: C, 48.62; H, 8.16; S, 21.63. Found: C, 48.99; H, 8.09; S, 21.30.

***t*-Butyl Carbazate from *t*-Butyl S-Methyl Thiolcarbonate.**—A mixture of 192.5 g. of *t*-butyl S-methyl thiolcarbonate and 72 g. of 64% hydrazine (Mathieson) was heated in an oil-bath at 105–110° (external temperature) with mechanical stirring for 24 hours under a reflux condenser. The resulting mixture was diluted with 250 ml. of methylene dichloride and solid magnesium sulfate added until the lower aqueous layer became nearly solid and non-flowing. The upper layer then was decanted, dried (magnesium sulfate) and the solvent removed by distillation from a water-bath with the aid of a water aspirator. The clear liquid which remained was cooled and yielded snow-white crystals, amount 144.5 g. (84%), m.p. 40–42° (lit.[2] m.p. 41–42°). The carbazate was quite pure as obtained but could be recrystallized with 90% recovery, m.p. 40–41°, from a 50–50 mixture of low- (b.p. 30–60°) and high-boiling (b.p. 60–90°) ligroin.

***t*-Butyl α-Bromoisobutyrate.**—A solution of 41.5 ml. of *t*-butyl alcohol and 35.2 ml. of pyridine in 100 ml. of methylene dichloride was cooled in an ice-bath with stirring while 100 g. of α-bromoisobutyryl bromide was added during 1.5 hours. The mixture was allowed to stir for four hours in the ice-bath and at room temperature for 15 hours, washed with three 75-ml. portions of water, dried (magnesium sulfate) and distilled, b.p. 35–37° (1.0 mm.), amount 67 g. (69%), λ_{max} 5.77 μ (C=O).

Anal. Calcd. for $C_8H_{15}O_2Br$: C, 43.06; H, 6.78; Br, 35.82. Found: C, 43.24; H, 6.49; Br, 35.79.

***t*-Butyl α-Nitroisobutyrate.**[29]—A solution of 22.3 g. of *t*-butyl α-bromoisobutyrate and 10.5 g. of sodium nitrite in 80 ml. of dimethyl sulfoxide was stirred at room temperature for 15 hours. The resulting mixture was diluted with water to 300 ml. and extracted with four 25-ml. portions of methylene dichloride. Distillation of the dried (magnesium sulfate) extracts gave 13.5 g. (71.4%) of the nitro ester, b.p. 36° (0.3 mm.). A center cut for analysis distilled through a 30-cm. helices-packed column had b.p. 39° (0.4 mm.), λ_{max} 5.74 μ (C=O).

Anal. Calcd. for $C_8H_{15}NO_4$: C, 50.78; H, 7.99; N, 7.40. Found: C, 51.03; H, 8.11; N, 7.25.

Formation of *t*-Butyl Carbazate from *t*-Butyl α-Nitroisobutyrate.—A mixture of 3.8 g. of the ester and 1.5 g. of 98% hydrazine was heated in an oil-bath (external temperature 98–100°) for 15 hours, diluted with 25 ml. of methylene dichloride, the mixture dried (magnesium sulfate) and the solvent removed to give 32% of the carbazate isolated as the benzal derivative,[2] m.p. and mixed m.p. 190–192° dec.

Formation of *t*-Butyl Carbazate from *t*-Butyl Trichloroacetate.—To a stirred solution of 15 ml. of 100% hydrazine hydrate in 40 g. of dimethylformamide there was added during 5–7 min. 22 g. of *t*-butyl trichloroacetate[30] which caused the reaction mixture to become hot. The mixture was stirred for 10 hours at room temperature, a solution of 40 g. of sodium hydroxide in 500 ml. of water was added and stirring continued for an additional 15 hours. Continuous extraction with ether gave 34% of the carbazate, isolated as the benzal derivative,[2] m.p. 190–192° dec.

Ethyl *t*-Butyl Carbonate. Procedure A.—A solution of potassium *t*-butoxide prepared from 20 g. of potassium and 500 ml. of *t*-butyl alcohol was treated with 400 ml. of benzene and carbon dioxide passed into the well-stirred mixture for about 30 min. There was added 75 ml. of dimethylformamide and 82.5 g. of ethyl bromide and the mixture refluxed with stirring for 48 hours. After the addition of 500 ml. of water the layers were separated and the organic layer washed twice with 250-ml. portions of water. Drying and distillation through a 30-cm. Vigreux column gave 24 g. (39%) of the carbonate, b.p. 140–143°.

Procedure B.—The carbonate was prepared more conveniently by reaction of ethyl chloroformate and sodium *t*-butoxide suspended in *t*-butyl alcohol. The yield was 56%, b.p. 140–141°.

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[22] E. H. White, THIS JOURNAL, **77**, 6011 (1955).

[23] J. E. Leffler and A. A. Bothner-By, *ibid.*, **73**, 5473 (1951).

[24] A. Hantzsch and A. Sauer, *Ann.*, **299**, 67 (1898).

[25] F. Tiemann and P. Kruger, *Ber.*, **17**, 1685 (1884).

[26] Melting points and boiling points are uncorrected.

[27] Elemental analyses are by Weiler and Strauss, Oxford, England.

[28] Infrared spectra of solids (Nujol mulls) and liquids (neat) were recorded linearly in wave length on a Perkin–Elmer Model 21 spectrophotometer, sodium chloride optics.

[29] The general synthesis of α-nitro esters of N. Kornblum, R. K. Blackwood and J. W. Powers [THIS JOURNAL, **79**, 2507 (1957)] was used.

[30] W. F. Scovill, R. E. Burk and H. P. Lankelma, *ibid.*, **66**, 1039 (1944).

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.10; H, 9.45.

***t*-Butyl Carbamate.**—A mixture of 150 g. of N-bromosuccinimide (Eastman Kodak Co., Pract. grade as received), 5 g. of allyl chloride, 0.1 g. of benzoyl peroxide and 750 ml. of dry chloroform was refluxed for 15 hours. The chloroform was removed by distillation from a water-bath with the aid of a water aspirator (80° (20 mm.)) and the residue distilled quickly from a water-bath through a Claisen flask. There was obtained 110 g. of crude isocyanate, b.p. 60–62° (3 mm.), which was added slowly (5–8 min.) with stirring and cooling to 200 ml. of *t*-butyl alcohol. After dilution with water to 1.3 l., cooling in an ice-bath and filtration there was obtained 139 g. (61.5%) of air-dried *t*-butyl N-β-bromopropionylcarbamate, m.p. 100–103° (lit.[31] m.p. 103–105°).

A solution of 93 g. of sodium hydroxide in 1500 ml. of water was heated on a hot-plate to 75–80° and 139 g. of *t*-butyl N-β-bromopropionylcarbamate added in one portion with stirring. The solid dissolved in 2–3 min. and the hot solution (85–90°) was filtered. The filtrate was cooled rapidly, first under tap water and then by standing in a refrigerator for several hours. Filtration gave 41.2 g. of pure *t*-butyl carbamate, m.p. 108–110° (lit.[7] m.p. 108–108.5°). Extraction of the filtrate with 6–7 15-ml. portions of methylene dichloride followed by evaporation of the extracts in a flat dish gave an additional 3 g. of the carbamate, m.p. 108.5–109.7°. The total yield was 44.2 g. (73%).

Ethyl *t*-Butyl Oxalate.—A solution of 35.2 g. of *t*-butyl alcohol and 37.6 g. of pyridine in 100 ml. of methylene dichloride was cooled in an ice-bath and 64.8 g. of ethoxalyl chloride[32] added with stirring over a period of one hour. The mixture was stirred in the ice-bath for 4 hours, at room temperature overnight, and then washed with two 50-ml. portions of water. Removal of solvent from the dried (magnesium sulfate) solution and then distillation gave 65.5 g. (79.4%) of the ester, b.p. 50–52° (1.25 mm.). A center cut for analysis had b.p. 48° (1.0 mm.), λ_{max} 5.66, 5.75 μ (C=O).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.43; H, 8.04.

Ethyl *t*-Amyl Oxalate.—The *t*-amyl ester was prepared as given above for the *t*-butyl derivative. The yield was 70%, b.p. 46° (0.3 mm.); λ_{max} 5.68, 5.76 μ (C=O).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.43; H, 8.61.

***t*-Butyl Oxamate.**—To a solution of 100 g. of ethyl *t*-butyl oxalate in 30 ml. of ethyl alcohol was added in 4–5 portions with swirling during 3–5 minutes 40 ml. of concentrated ammonium hydroxide. The solution was allowed to stand at room temperature for 12 hours and diluted with 200 ml. of methylene dichloride. The lower organic layer was separated and the upper layer extracted with 25 ml. of methylene dichloride. Upon removal of the solvent from the dried (magnesium sulfate) solution by means of a water aspirator and a water-bath, an oil remained which on cooling gave 68 g. (82%) of snow-white flakes, m.p. 77–82°, which were washed out with low-boiling (30–60°) ligroin. Recrystallization by dissolution in benzene, filtration and precipitation with 2–3 volumes of 60–90° ligroin gave 52 g. (62.5%) of the oxamate, m.p. 84–87°. The analytical sample (benzene–60–90° ligroin) had m.p. 89.5–90.5°; λ_{max} 5.71, 5.90 μ (C=O).

Anal. Calcd. for $C_6H_{11}O_3N$: C, 49.64; H, 7.64; N, 9.65. Found: C, 50.00; H, 7.71; N, 9.55.

***t*-Butyl Cyanoformate.**—To a mixture of 30 g. of *t*-butyl oxamate and 36.8 ml. of pyridine cooled in an ice-bath there was added dropwise over a 10-min. period with mechanical stirring 52 g. of trifluoroacetic anhydride. The ice-bath was removed and the thick mixture allowed to stir for 10 min. at room temperature after which 50 ml. of ether was added and the mixture stirred for an additional 5 min. There was added 65 ml. of water, the top layer separated and the aqueous layer extracted with three 30-ml. portions of ether. The combined ether layers were washed once with 50 ml. of water and twice with 35-ml. portions of 1 *M* sodium bicarbonate solution, dried (magnesium sulfate) and the ether removed by distillation from a water-bath (45°) with the aid of a water aspirator (150 mm.). The residue then was distilled at 64–65° (55 mm.), amount 20.5 g. (78%); λ_{max} 4.50 μ (C≡N), 5.72 μ (C=O).

Anal. Calcd. for $C_6H_9O_2N$: C, 56.68; H, 7.13; N, 11.02. Found: C, 57.12; H, 7.08; N, 10.55.

Acylations with *t*-Butyl Cyanoformate.—Comparison of the acylating ability of *t*-butyl cyanoformate with that of *t*-butyl azidoformate[3,6] shows that the cyano compound is more reactive but the initial products are less pure than those obtained from the azide which remains the carbo-*t*-butoxylating agent of choice. The use of triethylamine as a catalyst in the acylations involving the cyano compound led to the formation of intractable dark colored oils. Acylation of the following representative substances was examined:

(a) **Ammonia.**—A mixture of 1.27 g. of *t*-butyl cyanoformate, 10 ml. of concd. ammonium hydroxide and 5 ml. of water was allowed to stand at room temperature with occasional shaking for 12 hours (the reaction appeared complete within 2–3 hours). Filtration gave 1 g. (85.5%) of *t*-butyl carbamate as white needles, m.p. 108–110° (lit.[3] m.p. 108–108.5°).

(b) ***t*-Butyl Carbazate.**—A solution of 1.32 g. of *t*-butyl carbazate and 1.27 g. of the cyano compound in 2 ml. of dimethylformamide was allowed to stand at room temperature for 48 hours. Dilution with water gave 1.8 g. (77.5%) of cream-orange *t*-butyl hydrazodiformate, m.p. 122.5–124.5° (lit.[3] m.p. 124–125.5°). When *t*-butyl azidoformate was treated with the carbazate under the same conditions, less than 40% of the hydrazo compound was formed.

(c) **Phenylhydrazine.**—A solution of 0.01 mole of each of the reactants in 5 g. of methylene dichloride which was allowed to stand for one week at room temperature afforded 62% of *t*-butyl 2-phenylcarbazate, m.p. 91–93° (lit.[3] m.p. 92–93.5°).

(d) **Aniline.**—A mixture of 0.01 mole of each of the reactants was allowed to stand at room temperature for 4 days without solvent. Addition of water followed by dil. hydrochloric acid gave 45–55% of cream-white *t*-butyl carbanilate, m.p. 135.5–138° (lit.[3] m.p. 136.3–136.5°).

Benzoic Anhydride from Dibenzhydroxamic Acid.—A suspension of 2.4 g. of dibenzhydroxamic acid in 25 ml. of methylene dichloride was treated with a stream of oxides of nitrogen prepared from sodium nitrite and nitric acid according to the method of Bachmann and Hoffman.[33] The gas was passed into the mixture until the solid just dissolved (an excess of nitrous fumes should be avoided) and the greenish colored solution was washed once with 25 ml. of water, dried (magnesium sulfate) and the solvent removed with the aid of a water-bath and a water aspirator. The colorless oil solidified on cooling to 2 g. (88.5%) of crystalline white solid, m.p. 39.5–41.5°. Recrystallization from benzene–ligroin (60–90°) raised the m.p. to 41–43°; mixed m.p. with an authentic sample 41–43°. When the reaction was carried out by addition of solid sodium nitrite to a solution of the hydroxamic acid in 95% acetic acid the yield of anhydride was 43%.

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(31) Personal communication from Dr. H. W. Johnson (ref. 8) to whom we are indebted for an outline of the procedure described above for the reaction of the isocyanate with *t*-butyl alcohol. The β-bromopropionyl carbamate is sufficiently pure as obtained for the next step, but it may be recrystallized from methanol or methanol-water if desired (m.p. 102–104°).

(32) Large-scale preparations of ethoxalyl chloride are easily carried out by the method of K. Kindler, W. Metzendorf and Dschi-yin-Kwok [*Ber.*, **76**, 308 (1943)].

(33) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 249.