[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BOSTON UNIVERSITY]

Carbamates and N-Nitrocarbamates

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Fifteen new carbamates and eighteen new N-nitrocarbamates have been reported. Aliphatic and alicyclic carbamate can be nitrated smoothly and in excellent yield with fuming nitric acid and acetic anhydride to form N-nitrocarbamates. With aromatic carbamates the nitro group was usually found in the ring. This nitrating medium was ineffective or caused the formation of tars in the case of six heterocyclic carbamates. Two of these were successfully nitrated (ring nitration) with hot fuming nitric and concentrated sulfuric acids.

Ethyl N-nitro-N-isopropylcarbamate can be hydrolyzed readily in 10% sodium hydroxide solution or in 50% sulfuric acid. Ethyl N-nitro-N-isopropylcarbamate is oxidized to isopropyl-N-nitroamine in alkaline potassium permanganate solution, but is completely decomposed in acidic potassium permanganate solution and in fuming nitric acid.

N-Nitrocarbamates have previously been prepared by others[2] by nitration of either methyl or ethyl N-alkyl carbamates at 0° with 500–1700% excess of absolute or fuming nitric acid. We have found that a mixture of fuming nitric acid and acetic anhydride is a superior nitrating medium for N-alkylcarbamates, especially if the alkyl group contains a branched chain.

Most of the new carbamates listed in Table I were prepared by the reaction between an amine and an alkyl chloroformate. The new N-nitrocarbamates are listed in Table II.

Three new heterocyclic carbamates, ethyl N-[4-(1,2,4-triazolyl)]-carbamate (I), ethyl N-(2-thiazolyl)-carbamate (II) and ethyl N-(2-thenyl)-carbamate (III), and three previously described carbamates, ethyl N-(2-furfuryl)-carbamate (IV),[3] ethyl N-(2-pyridyl)-carbamate (V)[4] and ethyl N-(3-pyridyl)-carbamate (VI),[5] could not be nitrated successfully by fuming nitric acid in acetic anhydride. The original carbamate was recovered in the case of I, II, V and VI, and only a tarry mass was obtained in the case of III and IV. An attempt was made to nitrate IV in an alkaline medium using tetranitromethane and pyridine.[6] Although the pyridine salt of trinitromethane precipitated slowly, indicating a reaction, only a black tarry product was obtained. However, compounds V and VI were successfully nitrated by heating with a mixture of fuming nitric and concentrated sulfuric acids to form ethyl N-[2-(5-nitropyridyl)]-carbamate and ethyl N-[3-(2-nitropyridyl)]-carbamate, respectively.

A satisfactory product could not be obtained from the nitration of ethyl N-β-diethylaminoethylcarbamate. It decomposed extensively when distilled at 1 mm. and the distillate continued to evolve a gas on standing. An undistilled portion, washed free of acid, also evolved a gas.

No evidence was found in the literature to indicate that the nitration of ethyl N-phenylcarbamate had been attempted. Blanksma and Verberg[7] nitrated methyl and ethyl N-(3,5-dinitrophenyl)-carbamates with absolute nitric acid at −15° and obtained the corresponding N-nitro derivatives. Nitration of ethyl N-phenylcarbamate with fuming nitric acid in acetic anhydride at either +10° or −20° to −5° gave a mixture of ethyl N-*o*-nitrophenylcarbamate[8] and ethyl N-*p*-nitrophenylcarbamate[9] which was separated by steam distillation, the ortho isomer being volatile with steam, presumably as a result of chelate ring formation. Nitration of both above isomers with fuming nitric acid in acetic anhydride at temperatures not exceeding 25° gave ethyl N-(2,4-dinitrophenyl)-carbamate.[9]

An attempt to nitrate ethyl N-(2,4,6-trinitrophenyl)-carbamate[10] with fuming nitric acid in acetic anhydride at room temperature was unsuccessful, the starting material being recovered unchanged.

Ethyl N-mesitylylcarbamate[11] was nitrated using fuming nitric acid in acetic anhydride, at room temperature, but the product was difficult to purify. Better results were obtained with fuming nitric and concentrated sulfuric acids, the product being ethyl N-(3,5-dinitromesitylyl)-carbamate, the composition of which was proved by hydrolysis to be 3,5-dinitromesidine.[12] Ethyl N-(3,5-dinitromesitylyl)-carbamate was nitrated with absolute nitric acid[13] to yield ethyl-N-nitro-N-(3,5-dinitromesitylyl)-carbamate.

Ethyl N-nitro-N-isopropylcarbamate was hydrolyzed to the extent of 95% by refluxing for two hours with 10% sodium hydroxide solution or refluxing for six hours with 5% sodium hydroxide solution.

Refluxing ethyl N-nitro-N-isopropylcarbamate with 50% sulfuric acid solution for 3 hours caused hydrolysis to the extent of 95%; while only 80% was hydrolyzed after refluxing for one hour. Refluxing for 8 hours with 10% sulfuric acid solution caused only 29% hydrolysis.

Oxidation of ethyl N-nitro-N-isopropylcarbamate with alkaline potassium permanganate solution yielded the sodium salt of isopropyl N-nitroamine, sodium carbonate and sodium acetate. Quantitative analysis of the products accounted for 89% of the theoretical amounts of isopropyl-N-nitroamine and carbon dioxide.

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(1) Abstracted from a portion of the dissertation submitted by Howard M. Curry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) (a) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 258, 343 (1888); *ibid.*, **8**, 297 (1889). (b) J. Thiele and A. Lachmann, *Ber.*, **27**, 1520 (1894); *Ann.*, **288**, 287 (1895). (c) J. C. A. S. Thomas, *Rec. trav. chim.*, **9**, 69 (1890); (d) H. Van Erp, *ibid.*, **14**, 21 (1895); (e) H. J. Backer, *ibid.*, **31**, 12 (1912).

(3) W. Marckwald, *Ber.*, **23**, 3208 (1890).

(4) R. Camps, *Arch. Pharm.*, **240**, 350 (1902).

(5) S. W. Fox and H. Field, *J. Biol. Chem.*, **147**, 651 (1943).

(6) E. Schmidt and H. Fischer, *Ber.*, **53**, 1529 (1920).

(7) J. J. Blanksma and G. Verberg, *Rec. trav. chim.*, **53**, 1037 (1934).

(8) C. Rudolph, *Ber.*, **12**, 1295 (1879).

(9) H. Hager, *ibid.*, **17**, 2625 (1884).

(10) J. C. Crocker and F. H. Lowe, *J. Chem. Soc.*, **85**, 651 (1904).

(11) J. Eisenberg, *Ber.*, **15**, 1016 (1882).

(12) A. Ladenburg, *Ann.*, **179**, 168 (1875).

(13) F. C. Chattaway, *J. Chem. Soc.*, **97**, 2100 (1910).

TABLE I

PROPERTIES[a] OF CARBAMATES, $RNHCOOR'$ AND $R(NHCOOR')_2$

R	R′	Yield, %	B.p., °C.	Mm.	Density $^{20}_{20}$	Ref. index ^{20}D	Nitrogen, % Calcd.	Found
$(CH_3)_2CH$	C_2H_5	92	64 (174–175)	7 (760)	0.9548	1.4229	10.7	10.5
n-$C_{12}H_{25}$[b]	C_2H_5	90	M. 34–35	[c]			5.45	5.67
n-$C_{18}H_{37}$[b]	C_2H_5	84	M. 63	[d]			4.11	3.90
$(C_2H_5)_2N$–C_2H_4[e]	C_2H_5	75	90	3	0.9666	1.4481	14.9	14.6
ClC_2H_4[f]	C_2H_5	87	76–77	3	1.162	1.4536		
ClC_2H_4[g]	$(CH_3)_2CH$	73	88	3	1.115	1.4486	8.46	8.3
n-C_4H_9	n-C_4H_9	87	88	3	0.9238	1.4359	8.1	7.8
C_2H_5	n-C_4H_9	83	66	3	0.9413	1.4301	9.7	9.5
C_6H_{11}	C_2H_5	81	238–239	760(dec.)[h]				
o-$C_6H_{11}C_6H_{10}$	C_2H_5	61[i]	140–141	1	1.002(d^{50}_{20})	1.4805(n^{50}D)	5.54	5.56[j]
CH_2CH_2	C_2H_5[k]	88(crude)	M. 110–111(1)					
$C_9H_9N_2O_4$[s]	C_2H_5[l]	61	M. 180–181				14.1	13.8
$(CH_2)_4$	C_2H_5[m]		M. 94.1					
$(CH_2)_6$	C_2H_5[n]	98(crude)	M. 83–84(1)					
$CH_3CH(C_6H_5)$	C_2H_5	99[o]	113–115 M. 23–25	3			7.25	7.36
$C_2H_2N_3$[t]	C_2H_5	83	M. 184–186 (dec.)				35.9	36.0
C_3H_2NS[u]	C_2H_5	62	M. 153–154[d]				16.2	15.7
C_5H_5S[v]	C_2H_5[p]	87	149–150	9	1.172	1.5246	7.56	7.30
$C_5H_3N_2O_2$[w]	C_2H_5	46[q]	M. 209–210 (dec.)				19.9	19.3[r]
$C_5H_3N_2O_2$[x]	C_2H_5	61[q]	M. 83–84				19.9	19.7

[a] Additional physical properties for carbamates previously described in the literature are: methyl N-ethylcarbamate, n^{20}D 1.4205; ethyl N-n-propylcarbamate n^{20}D 1.4268, d^{20}_{20} 0.9538; ethyl N-t-butylcarbamate n^{20}D 1.4250, d^{20}_{20} 0.9370, b.p. 43° (1 mm.). [b] These amines were generously donated by the Chemical Division of Armour and Company. Because of the insolubility of octadecylamine in aqueous alkali, a hot solution of octadecylamine in benzene was emulsified by vigorous stirring with aqueous alkali before adding ethyl chloroformate. The carbamate was recrystallized twice from 95% ethyl alcohol. [c] Recrystallized from approximately 85% ethyl alcohol. [d] Recrystallized from 95% ethyl alcohol. [e] $(C_2H_5)_2NCH_2CH_2NH_2$ was generously donated by the Ciba Pharmaceutical Products Company. [f] Made from β-chloroethylamine hydrochloride, ethyl chloroformate and sodium hydroxide solution. Wenker (reference footnote g) made this compound from ethyl β-hydroxyethylcarbamate and thionyl chloride. [g] Made from isopropyl alcohol and 2-chloroethyl isocyanate, H. Wenker, THIS JOURNAL, **58**, 2608 (1936). [h] M. Barker, L. Hunter and N. G. Reynolds, *J. Chem. Soc.*, 874 (1948) reported m.p. 55–56°. After distillation, we found m.p. 58–59°. [i] The final reaction mixture was a sluggish, sticky mass which was extracted repeatedly with ether until the aqueous layer was clear and there was no further evidence of organic material in the flask. [j] Calculated for $C_{15}H_{27}NO_2$: C, 71.2; H, 10.67. Found: C, 71.5; H, 10.32. [k] Made by E. Fischer and H. Koch, *Ann.*, **232**, 228 (1885), from alcohol–ether solution of ethylenediamine and ether solution of ethyl chloroformate; also by Curtius, *J. prakt. Chem.*, [2] **52**, 222 (1895), from succinic acid azide. [l] Recrystallized from absolute ethyl alcohol. [m] Made from adipamide by Mr. Carlos M. Samour in this Laboratory. [n] Made by T. Curtius and H. Clemm, *Ber.*, **29**, 1167 (1896), from suberic acid azide. [o] Prior to distillation. [p] Made from 2-thenylamine, Hartough, Lukasiewicz and murray, THIS JOURNAL, **70**, 1146 (1948). [q] Prior to recrystallization. [r] Calculated for $C_9H_9N_3O_4$: C, 45.5; H, 4.3. Found: C, 46.0; H, 4.4. [s] Dinitromesityl. [t] 4-(1,2,4-Triazolyl). [u] 2-Imidazolyl. [v] 2-Thenyl. [w] 2-(5-Nitropyridyl). [x] 3-(2-Nitropyridyl).

Ethyl N-nitro-N-isopropylcarbamate and isopropyl-N-nitroamine were both oxidized readily by fuming nitric acid at room temperature.

Experimental

The preparation of ethyl N-isopropylcarbamate and ethyl N-nitro-N-isopropylcarbamate will serve to indicate the general procedures used. Variations are indicated at the end of these preparations or as footnotes to the appropriate tables.

Ethyl N-Isopropylcarbamate.—One hundred and forty-seven grams (3.68 moles) of sodium hydroxide was dissolved in 200 cc. of water and placed in a two-liter, three-necked flask equipped with a mechanical stirrer, a dropping funnel and a thermometer. The mixture was cooled to 0° by means of an ice–salt-bath or Dry Ice–acetone-bath and 189 g. (3.20 moles) of isopropylamine was added. Then 327 g. (3 moles) of ethyl chloroformate was added through the dropping funnel at such a rate that the temperature did not rise above 20°. When addition was complete the stirring was continued for a few minutes and the ethyl N-isopropylcarbamate was drawn off in a separatory funnel and dried over anhydrous potassium carbonate. The product was then distilled *in vacuo*.

In some cases, especially when there were fewer than six carbon atoms in the carbamate, the carbamate was extracted with ether and the ether solution dried over anhydrous potassium carbonate.

Ethyl N-Nitro-N-isopropylcarbamate.—Six hundred and thirty-six grams (6.23 moles) of acetic anhydride was placed in a two-liter, three-necked flask equipped with a mechanical stirrer, a dropping funnel and a thermometer. The flask was cooled by means of an ice–salt-bath and 325 g. (4.50 moles, 218 cc.) of fuming nitric acid (sp. gr. 1.49) was added from the dropping funnel at such a rate that the temperature did not rise above 10°. When addition was complete, 393 g. (3 moles) of ethyl N-isopropylcarbamate was added from the dropping funnel. The rate of addition was controlled so that the temperature was maintained in the range 20–30°. After all of the carbamate had been added, the temperature was allowed to fall to 0° and the mixture was poured into two liters of water. The nitrocarbamate separated as an oil and was drawn off in a separatory funnel. The oil was washed repeatedly with 10% potassium carbonate solution until free from acid (litmus test), dried by filtering twice through two thicknesses of filter paper, and then distilled under reduced pressure.

In some cases, especially when there were fewer than six carbons in the carbamate, the nitrocarbamate–water mixture was extracted with ether, the ether layer washed with water and 10% potassium carbonate solution and then dried over anhydrous magnesium sulfate.

Ethyl N-*t*-Butylcarbamate.—This compound was prepared from t-butylamine and ethyl chloroformate in 93% yield. It was also prepared as follows from trimethylacetamide by means of the Hofmann rearrangement.[14] A solution obtained by adding 9.11 g. (0.396 mole) of sodium to

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(14) E. S. Wallis and J. F. Lane, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 282.

TABLE II

PROPERTIES OF N-NITROCARBAMATES, $RN(NO_2)COOR'$ AND $R[N(NO_2)COOR']_2$

R	R′	Yield, %	B.p., °C.	B.p., Mm.	Density$^{20}_{20}$	Ref. index^{20}D	Nitrogen, % Calcd.	Nitrogen, % Found
C_2H_5	CH_3	80	72	11	1.233	1.4483	18.9	18.6
C_2H_5	C_2H_5	86	107	31	1.163	1.4432	17.3	17.1
C_3H_7	C_2H_5	78	66	3	1.123	1.4431	15.9	15.6
$(CH_3)_2CH$	C_2H_5	86	72	7	1.112	1.4381	15.9	15.7
$(CH_3)_3C$[a]	C_2H_5	52	56	2(dec.)	1.051	1.4331	14.7	14.8
n-$C_{12}H_{25}$	C_2H_5	98	Not distillable		0.9780	1.4545	9.2	8.9
n-$C_{18}H_{37}$	C_2H_5	98	M. 38-39[b]				7.25	7.2
$ClCH_2CH_2$	C_2H_5	72	95	3	1.320	1.4710	14.3	14.2
$ClCH_2CH_2$	iso-C_3H_7	90	96	3	1.251	1.4633	13.3	12.8
n-C_4H_9	n-C_4H_9	76	98	3	1.048	1.4480	12.8	12.8
C_2H_5	n-C_4H_9	68	79	3	1.091	1.4455	14.7	14.7
C_6H_{11}	C_2H_5	64	120–122	7[c]	1.078	1.4639	12.95	12.65[d]
o-$C_6H_{11}C_6H_{10}$	C_2H_5	89	Not distillable		1.072	1.4901[e]	9.4	9.0
$C_9H_9N_2O_4$	C_2H_5	33[f]	M. 142–143				16.3	15.9
$C_6H_5CH_2$	C_2H_5	92	Dec. while distilling[g]		1.213	1.5203	12.5	11.9
$CH_3CH(C_6H_5)$	C_2H_5	89	Dec. 190 (1 mm.)[h]		1.197	1.5233	11.7	10.3
$(CH_2)_2$	C_2H_5[i]	99(crude)	M. 83–84					
$(CH_2)_4$	C_2H_5	81	M. 55[j]				18.0	17.9
$(CH_2)_6$		96	Not distillable[f]		1.221	1.4762	16.0	15.8

[a] Van Erp[4] was unable to nitrate this carbamate. [b] Recrystallized from 95% ethyl alcohol. [c] Distilled with the aid of boiling stones only, since a stream of air caused oxidative decomposition. [d] Calculated for $C_9H_{16}N_2O_4$: C, 50.0; H, 7.41. Found: C, 50.19; H, 7.62. [e] For comparison with the carbamate, the density and refractive index were determined at 50°, d^{50}_{20} 1.063, n^{50}D 1.4817. [f] The yield of crude product, m.p. 134–136° was 98%. [g] Physical constants and analyses determined with sample which was dissolved in ether, washed with 10% potassium carbonate solution until free from acid, then washed with water, dried over anhydrous potassium carbonate or magnesium sulfate and the last traces of ether removed under reduced pressure. [h] Although analytical data are unsatisfactory, the compound reacted with morpholine to form the morpholine salt of α-phenylethyl-N-nitroamine which gave a satisfactory analysis. H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5041 (1951). [i] Made by Franchimont and Klobbie[1a] using absolute nitric acid. [j] Recrystallized from aqueous alcohol by melting 7 g. of crude product with 100 cc. of boiling water and adding 190 cc. of hot ethyl alcohol, then filtering the hot solution.

200 cc. of absolute ethyl alcohol was cooled to 5° and 20 g. of trimethylacetamide was dissolved with vigorous stirring in this cold solution. Then 31.7 g. (0.198 mole) of bromine was added rapidly from a dropping funnel, causing the temperature to rise to 70°. After above five minutes, the mixture was cooled, filtered, and the alcohol removed by distillation. The dark brown oily residue was taken up in ether, filtered, the solid sodium bromide washed twice with ether and the combined ether extracts distilled. The remaining oil distilled at 72° (16 mm.); weight 8.6 g. (30%).

Ethyl N-[4-(1,2,4-(Triazolyl)]-carbamate.—4-Amino-1,2,-4-triazole[15] (12.38 g., 0.147 mole) was placed in a 600-cc. beaker and 9 g. (0.08 mole) of ethyl chloroformate was added. The temperature of the mixture rose slowly for about two minutes and then a vigorous exothermic reaction took place, causing the mixture to liquefy. After another minute the reaction was complete and the mixture resolidified. The solid was dissolved with gentle warming in 150 cc. of absolute ethyl alcohol, the 4-amino-1,2,4-triazole hydrochloride was precipitated by the addition of 200 cc. of ether and removed by suction filtration. The filtrate was then concentrated to a volume of 30 cc. by distillation on the steam-bath. On cooling, ethyl N-[4-(1,2,4-triazolyl)]-carbamate separated as fine white needles; weight 5.5 g. (48%). Evaporation of the filtrate yielded an additional 4.1 g. to give a total yield of 9.6 g. (83.5%).

Ethyl N-[2-(5-Nitropyridyl)]-carbamate.—A nitrating mixture was prepared from 11.9 g. (8 cc., 0.165 mole) of fuming nitric acid (sp. gr. 1.49) and 14.7 g. (8 cc., 0.150 mole) of concentrated sulfuric acid. Then 4 g. (0.024 mole) of ethyl N-(2-pyridyl)-carbamate[4] was added and the mixture was heated on the steam-bath under a reflux condenser for 1.5 hours, and then poured into 80 cc. of ice-water. The white powdery solid which precipitated was removed by suction filtration and dried in a vacuum desiccator. Unlike the original carbamate, this substance was found to be quite insoluble in water and hot ethyl alcohol. It was recrystallized from a mixture of three parts of benzene and one of ethyl acetate.

When the filtrate from the original nitration mixture was rendered basic with 20% sodium hydroxide solution, 0.97 g. of a white solid precipitated, which melted at 104–105° after recrystallization from ethyl alcohol. A mixed melting point determination of this material with the original carbamate showed no depression.

Identification of Ethyl N-[2-(5-Nitropyridyl)]-carbamate.—To a solution of 1.5 g. of sodium hydroxide in 5 cc. of water and 7 cc. of ethyl alcohol was added 0.73 g. of ethyl N-2-(5-nitropyridyl)-carbamate and the mixture was refluxed for one hour. The solution was then transferred to a small beaker and the lower layer of aqueous alkali was removed with a medicine dropper. The solution was then cooled in an ice-bath and yellow powdery crystals separated and were recrystallized from a mixture of 6 cc. of ethyl alcohol and 2 cc. of water; weight, 0.21 g. (43%). The light yellow solid, 5-nitro-2-aminopyridine, melted at 187°. Tschitschibabin[16] reported 188° as the melting point.

Ethyl N-[3-(2-Nitropyridyl)]-carbamate.—Four grams of ethyl N-(3-pyridyl)-carbamate[5] was nitrated using the procedure described for ethyl N-(2-pyridyl)-carbamate. The product was recrystallized twice from a mixture of 12 cc. of ethyl alcohol and 15 cc. of water. A mixture of this compound with the original carbamate melted over the range 61–69°.

Identification of Ethyl N-[3-(2-Nitropyridyl)]-carbamate.—Ethyl N-[3-(2-nitropyridyl)]-carbamate (1.65 g.) was suspended in 5 cc. of water and 10 cc. of 10% sodium hydroxide solution was added. The yellow solid dissolved in the alkali to yield a bright red solution. After standing about one hour at room temperature a few flaky yellow crystals made their appearance and 12 hours later the solution contained a yellow crystalline mass; weight 0.62 g. (57%), m.p. 180–184°. The yellow solid was recrystallized from aqueous ethyl alcohol to yield 0.48 g. of 2-nitro-3-aminopyridine melting at 195–196°. *Anal.* Calcd. for $C_5H_5N_3O_2$: N, 30.1. Found: N, 29.6.

One gram of 2-nitro-3-aminopyridine, suspended in a mix-

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[15] C. F. H. Allen and A. C. Bell, "Org. Syntheses," Vol. XXIV, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 12.

[16] A. E. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, **46**, 1236 (1914); *C. A.*, **9**, 1902 (1915). 3-Nitro-2-aminopyridine, which might have been expected, melts at 162° (Tschitschibabin).

ture of 5 cc. of 95% ethyl alcohol and 37 cc. of 10% sodium hydroxide solution, was reduced with 4 g. of Raney nickel-aluminum alloy using Ziegler's procedure,[17] m.p. 113–114°, identical with Ziegler's melting point for 2,3-diaminopyridine.

Nitration of Ethyl N-Phenylcarbamate.—Ten grams (0.06 mole) of ethyl N-phenylcarbamate was nitrated with 6.4 g. (0.09 mole) of nitric acid (sp. gr. 1.49) and 11.5 g. of acetic anhydride in the usual way. After pouring the mixture into 100 cc. of water, the resulting pale yellow solid was removed by suction filtration, washed twice with 10% potassium carbonate solution, once with water, and dried *in vacuo;* weight 13 g. (100%). The solid was recrystallized from 30 cc. of 95% ethyl alcohol to yield 3.2 g. of lemon yellow needles which melted at 51–54°. This was undoubtedly ethyl N-*o*-nitrophenylcarbamate, m.p. 58°.

Evaporation of the filtrate yielded 9 g. of solid which was recrystallized from 40 cc. of absolute ethyl alcohol to yield 3 g. of yellow needles, m.p. 49–75°. This melting point range suggested that the solid was probably a mixture of ortho and para isomers.

This solid was subjected to steam distillation. The distillate was bright yellow until about 250 cc. of distillate was obtained. On cooling, 0.7 g. of fine yellow crystals was obtained, m.p. 55–57°. A mixed melting point determination with a sample of ethyl N-*o*-nitrophenylcarbamate made from *o*-nitroaniline and ethyl chloroformate,[8] showed no depression. When the residue in the distilling flask was cooled, 0.7 g. of faint yellow crystals was obtained, m.p. 128–129°. A mixed melting point determination with ethyl N-*p*-nitrophenylcarbamate[18] showed no depression.

Ethyl N-(3,5-Dinitromesitylyl) Carbamate.—Ethyl N-mesitylyl carbamate was made from mesitylene by nitration,[19] reduction[20] and reaction with ethyl chloroformate.[11] This last reaction was also carried out by our usual method of allowing equimolecular amounts of mesidine and ethyl chloroformate to react in the presence of a sufficient quantity of alkali to neutralize the hydrogen chloride formed. The yield of crude product was practically 100%.

Three grams (0.0145 mole) of ethyl N-mesitylylcarbamate was dissolved in 4 cc. of concd. sulfuric acid and cooled to 0°. Then 1.89 g. (0.03 mole) (1.46 cc.) of fuming nitric acid (sp. gr. 1.49) was added dropwise, keeping the temperature below 10°. When addition was complete, the mixture was removed from the ice-bath and allowed to stand at room temperature for 15 minutes, at the end of which time it was poured onto 40 g. of cracked ice. This caused precipitation of a cream colored solid which was removed by suction filtration, washed twice with water and dried *in vacuo.* The product was recrystallized twice from ethyl alcohol (95%).

Hydrolysis of Ethyl N-(3,5-Dinitromesitylyl)-carbamate.—One gram of sodium hydroxide was dissolved in a mixture of 5 cc. of water and 7 cc. of ethyl alcohol. Then 0.7 g. of ethyl N-(3,5-dinitromesitylyl)-carbamate was added and the mixture was refluxed for one hour, during which time it changed from colorless to light yellow. The mixture was transferred to a small beaker and the top alcoholic layer was removed with a medicine dropper and set aside to cool. The product separated as yellow leaflets, weighing 0.31 g. (59%), m.p. 189–191°. Recrystallization from ethyl alcohol yielded 0.18 g. of 3,5-dinitromesidine, melting at 194–199°. Ladenburg[12] reported 193–194°.

Ethyl N-Nitro-N-(3,5-dinitromesitylyl)-carbamate.—Fifteen cc. (22.6 g., 0.358 mole) of absolute nitric acid[13] (sp. gr. 1.54) was cooled by means of an ice–salt-bath and 1.75 g. (0.006 mole) of ethyl N-(3,5-dinitro-2,4,6-mesitylyl)-carbamate was added in small portions. The reaction was not very exothermic and the mixture was allowed to warm to room temperature (23°) and stand for 20 minutes. The reaction mixture was then poured into 40 cc. of ice–water, which caused separation of a white, powdery precipitate. This was removed by suction filtration and dried in a vacuum desiccator. The product was recrystallized three times from ethyl acetate and washed with petroleum ether.

Alkaline Hydrolysis of Ethyl N-Nitro-N-isopropylcarbamate.—Approximately 10 g. of ethyl N-nitro-N-isopropylcarbamate was weighed accurately from a weighing bottle into a 500-cc. round-bottomed flask containing 100 cc. of 10% sodium hydroxide solution and equipped with a reflux condenser. After refluxing for two hours, the reaction mixture was cooled and transferred quantitatively to a 200-cc. volumetric flask and diluted to volume. Fifty-cc. aliquot portions were used for the titrations. Dilute hydrochloric acid (approximately 8%) was used for the titration to the phenolphthalein end-point to give a solution containing both sodium bicarbonate and the sodium salt of isopropyl-N-nitroamine. Titration with standard 0.4531 *N* hydrochloric acid to the methyl orange end-point liberated both carbon dioxide and isopropyl-N-nitroamine. The correctness of the titration procedure with respect to isopropyl-N-nitroamine was demonstrated by dissolving a weighed sample of the nitroamine in an excess of alkali, titrating first to the phenophthalein end-point and then to the methyl orange end-point. The purity of the isopropyl-N-nitroamine was 98% as determined by this procedure.

Acid Hydrolysis of Ethyl N-Nitro-N-isopropylcarbamate.—The procedure was the same as for the alkaline hydrolysis, except that 100 cc. of 50% sulfuric acid solution was used and the top of the reflux condenser was connected in series to four eight-inch test-tubes, each containing 40 cc. of 35% sodium hydroxide solution to absorb the liberated carbon dioxde. Isopropyl-N-nitroamine remained in the acid solution.

Oxidation of Ethyl N-Nitro-N-isopropylcarbamate with Alkaline Potassium Permanganate.—A solution containing 100 g. (0.63 mole) of potassium permanganate and 29 g. (0.73 mole) of sodium hydroxide dissolved in 625 cc. of water was placed in a one-liter three-necked flask equipped with a mercury-sealed stirrer, a thermometer and reflux condenser. The mixture was cooled in an ice-bath and 25 g. (0.14 mole) of ethyl N-nitro-N-isopropylcarbamate was added. The temperature remained below 5° for 15 minutes so the ice-bath was removed. The temperature rose gradually to 30°, and then began to rise so rapidly that the ice-bath was used to cool the reaction mixture. At about 50° there was a rapid precipitation of hydrated manganese dioxide. The ice-bath was removed and the mixture was stirred for about one hour, at which time the mixture had returned to room temperature and the reaction was considered complete. The manganese dioxide was filtered off and the filtrate decolorized by adding sodium bisulfite solution. After filtering again, the solution was evaporated to a volume of about 400 cc. This was transferred to a 500-cc. volumetric flask and diluted to 500 cc. Two 50-cc. aliquots were titrated with dilute hydrochloric acid to the phenolphthalein end-point. The resulting data indicated that 89% of the theoretical weights of carbon dioxide and isopropyl-N-nitroamine were obtained.

In one experiment, after removing the manganese dioxide and decolorizing the solution, concentrated hydrochloric acid was added until the solution was acid to methyl orange. It was then extracted with three 100-cc. portions of ether, the ether removed on a steam-bath and the remaining liquid distilled under reduced pressure. After the distillation of some water and acetic acid, 9 g. of isopropyl-N-nitroamine distilled at 89° at 8 mm.[2c] This compound was further identified by making the morpholine salt of isopropyl-N-nitroamine, m.p. 69–71°.[21]

In another experiment, the alkaline filtrate from the oxidation was acidified (to methyl orange) with sulfuric acid and distilled. The distillate contained acetic acid as was shown qualitatively by a positive basic ferric acetate test.

Oxidation of Ethyl N-Nitro-N-isopropylcarbamate and Isopropyl-N-nitroamine with Fuming Nitric Acid.—Although there is no evidence of any reaction between ethyl N-nitro-N-isopropylcarbamate (2 g.) and fuming nitric acid (2–4 cc.) at 0–5°, a vigorous exothermic reaction occurs at 20°. Isopropyl-N-nitroamine reacted similarly with fuming nitric acid. No attempt was made to isolate the reaction products.

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[17] J. B. Ziegler, THIS JOURNAL, **71**, 1891 (1949).

[18] Ethyl N-*p*-nitrophenylcarbamate was made by Rudolph's method[8] for ethyl N-*o*-nitrophenylcarbamate, using dioxane as solvent instead of chloroform.

[19] G. Powell and F. R. Johnson, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 449.

[20] R. Fittig and J. Storer, *Ann.*, **147**, 3 (1868).

[21] H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5041 (1951).