[CONTRIBUTION NO. 2616 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

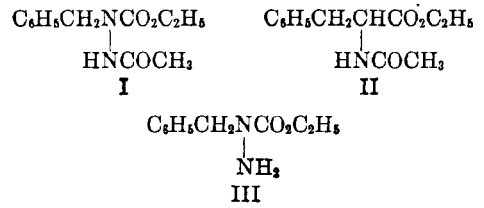
Synthesis and Properties of Ethyl 1-Acetyl-2-benzyl Carbazate, an Analog of Acetyl-D- and L-Phenylalanine Ethyl Ester[1]

ABRAHAM N. KURTZ AND CARL NIEMANN[2]

Received August 29, 1960

Several synthetic routes to ethyl 1-acetyl-2-benzyl carbazate have been investigated, its cyclization to 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 has been noted and a procedure for conversion of the latter compound to the former has been developed.

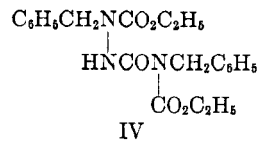
Ethyl 1-acetyl-2-benzyl carbazate (I), an analog of acetyl-D- and L-phenylalanine ethyl ester (II), was of interest to us because of its possible use in

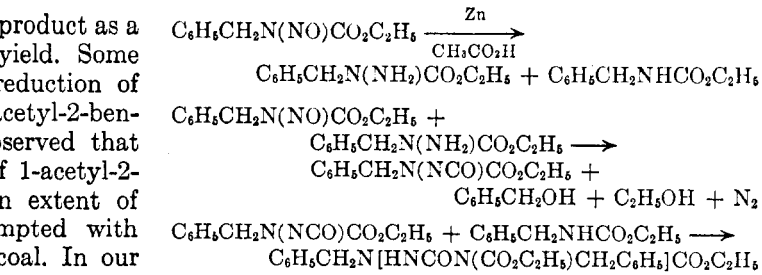


enzymatic studies. While this compound had not been prepared previously it might appear that it would be readily available by acetylation of the known ethyl 2-benzyl carbazate[3] (III). However, the route of the latter compound—i.e., ethyl carbazate → monohydrazone of ethyl carbazate and diacetyl → ethyl 1-diacetylidene-2-benzyl carbazate → ethyl 2-benzyl carbazate[3]—was sufficiently unattractive to cause us to explore other routes to its *N*-acetyl derivative. Three alternate procedures were considered. One involved the sequence, acethydrazide → 1-acetyl-2-benzylidenehydrazine → 1-acetyl-2-benzylhydrazine → ethyl 1-acetyl-2-benzyl carbazate; the second, the sequence benzylamine → benzylurethane → *N*-nitrosobenzylurethane → ethyl 2-benzyl carbazate → ethyl 1-acetyl-2-benzyl carbazate; and the third, the sequence 1-acetyl-2-benzyl hydrazine → 2-methyl-4-benzyl-1,3,4-oxidazolone-5 → ethyl 1-acetyl-2-benzyl carbazate.

The first procedure gave the desired product as a viscous, colorless oil, in reasonable yield. Some difficulty was experienced with the reduction of 1-acetyl-2-benzylidenehydrazine to 1-acetyl-2-benzylhydrazine. Schlogl *et al.*,[4] had observed that hydrogenolysis of the C = N bond of 1-acetyl-2-benzylidenehydrazine proceeded to an extent of 95% when the reduction was attempted with hydrogen over 10% palladized charcoal. In our initial experiments, with hydrogen over palladium black, we obtained a low melting product that was grossly contaminated with acethydrazide and was difficult to purify. However, conditions were found that resulted in a marked diminution in the extent of hydrogenolysis and a satisfactory intermediate was then obtained.

The second procedure encountered difficulty in the attempted reduction of *N*-nitrosobenzylurethane to ethyl 2-benzyl carbazate. With hydrogen over palladium, or platinum black, benzylurethane was obtained in yields greater than 95%, even when the hydrogenation was conducted at 25°. Reduction with zinc and acetic acid, which has been used successfully for the conversion of *sec*-arylalkylnitrosoamines to hydrazines,[5] gave a product in high yield that was clearly neither ethyl 2-benzyl carbazate or its *N*-acetyl derivative, but which could be hydrolyzed to ethyl 2-benzyl carbazate and benzylurethane with concentrated hydrochloric acid. Further examination of the product indicated that it was β-*N*-benzyl-β-*N*-carbethoxy-*N'*-benzyl-*N'*-carbethoxycarbamylhydrazine (IV), whose formation may be rationalized on the basis of the following reactions:





The preceding set of reactions is interesting and deserves attention. However, their existence discouraged further attempts to obtain ethyl 2-benzyl carbazate and ethyl 1-acetyl-2-benzyl carbazate by

(1) Supported in part by a grant from the National Institutes of Health, U. S. Public Health Service.

(2) To whom inquiries regarding this article should be sent.

(3) K. Ronco and H. Erlenmeyer, *Helv. Chim. Acta*, **39**, 1045 (1956).

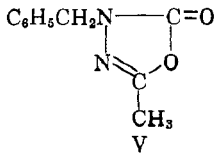
(4) K. Schlogl, J. Derkosch, and E. Wawersich, *Monatsh.*, **85**, 607 (1954).

(5) W. W. Hartman and L. J. Roll, *Org. Syntheses*, Coll. Vol. II, 418 (1943).

reduction of *N*-nitrosobenzyl urethane even though the former compound was obtained by a new route.

The isocyanate $C_6H_5CH_2N(NCO)CO_2C_2H_5$ postulated as one of the products of the reaction of *N*-nitrosobenzylurethane with ethyl 2-benzyl carbazate is a member of a class of compounds, of the type RN(NCO)COR′, where R may be hydrogen alkyl, or aryl, and R′, alkyl, aryl, alkoxy, etc., that, under other circumstances, are probable intermediates in the formation of heterocyclic systems such as the 1,3,4-oxadiazol-5-ones. Thus, a Hofmann rearrangement of *N*-benzoylurea gave 2-phenyl-1,3,4-oxadiazolone-5 in 40% yield.[6]

The attempted distillation of ethyl 1-acetyl-2-benzyl carbazate at 0.1 mm. and a maximum bath temperature of 125°, gave ethanol and 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 (V). The thermal cyclization of 1-acyl carbazates was first noted by



V

Rupe and Gebhardt,[7] who obtained 2-methyl-4-phenyl-1,3,4-oxadiazolone-5 upon attempted distillation of ethyl 1-acetyl-2-phenyl carbazate. Since 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 had not been described previously it was also synthesized by the procedure of Lieser and Nischk.[8] The products obtained by the two procedures were identical.

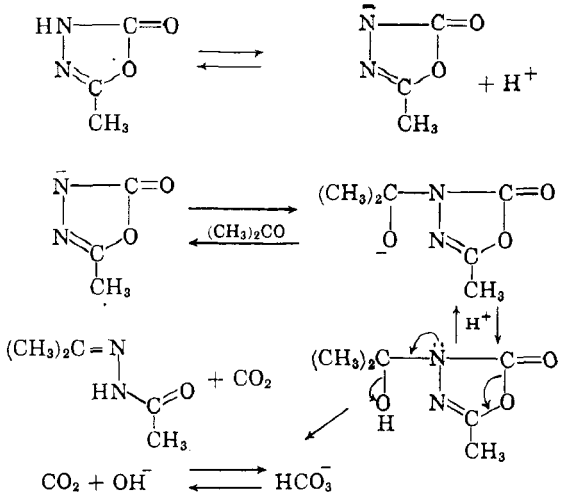
Ethyl 1-acetyl-2-benzyl carbazate and 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 may be distinguished on the basis of their infrared spectra. With the cyclic compound the N—H frequency is absent and the C=O frequency is shifted from 1718 and 1689 cm.$^{-1}$ to 1795 cm.$^{-1}$, a feature associated with the formation of a five membered cyclic lactam. Absorption at 1642 and 1314 cm.$^{-1}$ appears only in the cyclic compound and may be ascribed to C=N and C—O—C stretching frequencies. The pattern of the three frequencies that appear in 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 at 1437, 1393, and 1314 cm.$^{-1}$ is maintained in 2-methyl-1,3,-4-oxadiazolone-5[9] which has the same ring system, but differs only in that the benzyl group in the 4-position is replaced by hydrogen. Ethyl 1-acetyl-2-benzyl carbazate—*i.e.*, the acyclic molecule—possesses three strong bands at 1441, 1408, and 1379 cm.$^{-1}$ However, the C—O—C stretching frequency, that appears in the two cyclic derivatives at 1314 and 1321 cm.$^{-1}$ respectively, was conspicuously absent in the acyclic molecule. All three compounds exhibit symmetrical C—CH_3 C—H deformation frequencies at 1379 cm.$^{-1}$, 1390 cm.$^{-1}$, and 1393 cm.$^{-1}$.

The refractive index of 2-methyl-4-benzyl-1,3,4-oxadiazolone-5, n_D^{25} 1.5337, is greater than that of ethyl 1-acetyl-2-benzyl carbazate, n_D^{25} 1.5173.

2-Methyl-4-benzyl-1,3,4-oxadiazolone-5 is an analog of 2-methyl-4-benzyloxazolone-5, a member of a class of compounds that are readily solvolyzed at room temperature to the corresponding α-acylamino acid derivative.[10] However, the oxadiazolone is far more resistant to solvolysis than is the oxazolone. It was necessary to heat 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 with ethanolic sodium ethoxide at refluxing temperature to obtain ethyl 1-acetyl-2-benzyl carbazate in good yield in a reasonable time.

Since 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 can be prepared from 1-acetyl-2-benzylhydrazine ethanolysis of the former compound provides a third route to ethyl 1-acetyl-2-benzyl carbazate.

2-Methyl-4-benzyl-1,3,4-oxadiazolone-5, a neutral compound in water, can be recovered unchanged from an aqueous-acetone solution. However, 2-methyl-1,3,4-oxadiazolone-5, an acidic compound of $pK'_A = 7.93 \pm 0.02$ in water, dissolves in aqueous-acetone to give an acidic solution which, after initial neutralization to *p*H 7.9 requires the continual addition of base to maintain the *p*H at the above value. It is probable that the following reactions are responsible for the instability of 2-methyl-1,3,4-oxadiazolone-5 in aqueous acetone.



The above situation is reminiscent of the Erlenmeyer-Plochl reaction[10] except that in the present case the reaction proceeds under far milder conditions, probably because of the instability of the cyclic adduct and because of the driving force accompanying the formation of bicarbonate anion.

The behavior of 2-methyl-1,3,4-oxadiazolone-5 noted above suggests that in certain circumstances this compound would not only be a useful buffer in the region of *p*H 8 but if desired, could be de-

(6) V. M. Rodinov and V. V. Kiseleva, *Izvest. Nauk Akad. S.S.S.R. Odtel. Khim. Nauk* 57 (1951) [*Chem. Abstr.*, **46**, 4661 (1952)].

(7) H. Rupe and H. Gebhardt, *Ber.*, **32**, 10 (1899).

(8) T. Lieser and G. Nischk, *Ber.*, **82**, 527 (1949).

(9) A. Dornow and K. Brunecken, *Ber.*, **82**, 121 (1949).

(10) H. E. Carter, *Org. Reactions*, 198 (1946).

stroyed *in situ* by the simple addition of an aldehyde or ketone, preferably one yielding an insoluble hydrazone. The need for a buffer with these characteristics has been encountered previously.[11]

EXPERIMENTAL

Acethydrazide. One mole (88 g.) of ethyl acetate, 50.3 g. (1 mole) of hydrazine hydrate, and 50 ml. of ethanol were heated under refluxing conditions for 20 hr. The reaction mixture was evaporated to dryness and the residue recrystallized twice from a mixture of ethyl ether and chloroform to give the hygroscopic product in 65% yield; m.p. 64–66°, lit.,[12] m.p. 67°.

To 4.1 g. of acethydrazide in 75 ml. of benzene was added, slowly and with stirring, a solution of 6.7 g. of redistilled phenylisocyanate in 35 ml. of benzene. The reaction mixture was heated under refluxing conditions and with stirring for 1.5 hr., the precipitate collected, washed with hexane and recrystallized, first from 95% ethanol and then from a 4:1 mixture of hexane and recrystallized, first from 95% ethanol and then from a 4:1 mixture of hexane and ethanol to give 30% of 1-acetyl-4-phenyl semicarbazide, m.p. 174.7–175.2°, lit.,[13] m.p. 169°.

Anal. Calcd. for $C_9H_{11}N_3O_2$ (193): C, 56.0; H, 5.7; N, 21.8. Found: C, 55.7; H, 5.8; N, 22.0.

A solution of 0.65 g. of acethydrazide, 5 ml. of acetone and 1 drop of acetic anhydride was heated under refluxing conditions for 2 min., the reaction mixture cooled, the precipitate collected and recrystallized from aqueous ethanol to give 1-acetyl-2-isopropylidene hydrazine, m.p. 136.5–138.0°.

Anal. Calcd. for $C_5H_{10}N_2O$ (114): C, 52.6; H, 8.8; N, 24.6. Found: C, 52.5; H, 8.7; N, 24.5.

Infrared spectrum in chloroform: N—H, 3344 cm.$^{-1}$ (m); C=O, 1681, 1667, 1639 cm.$^{-1}$ (triplet).

1-Acetyl-2-benzylidene hydrazine. Redistilled benzaldehyde, 53 g. (0.5 mole) was added, in small portions and with vigorous shaking, to an ice cold solution of 37 g. (0.5 mole) of acethydrazide in 100 ml. of water. The reaction mixture was maintained at 5° for 2 days, the precipitate collected, washed with water, dried, and then washed with ethyl ether to remove the yellow benzalazine impurity. The colorless product was recrystallized from aqueous ethanol to give 1-acetyl-2-benzylidene hydrazine in 66% yield. M.p. 139–141°, lit.,[14] 134°.

Ultraviolet spectrum in 95% ethanol: λ_{max} = 280 mμ, ϵ = 16,700, λ_{max} = 303 mμ, ϵ = 10,000. For benzalazine in 95% ethanol: λ_{max} = 299 mμ, ϵ = 26,800; λ_{max} = 312 mμ, ϵ = 23,600.

Palladium catalyst. The catalyst is essentially that of Willstätter and Waldschmidt-Leitz.[15] Palladium chloride, 10 g., was dissolved in 150 ml. of distilled water containing 5 ml. of concd. hydrochloric acid and 71 ml. of 36–38% formaldehyde. The reaction mixture was placed in a bath maintained at −10° and 142 ml. of 50% aqueous potassium hydroxide was added with vigorous stirring and at a rate so as to keep the temperature below 3°. The mixture was then heated to 60°, stirred for 15 min., cooled to room temperature and washed with distilled water by decantation, until the washings were neutral and free of chloride ion. The catalyst was stored under distilled water.

1-Acetyl-2-benzylhydrazine. A solution of 10 g. (0.062 mole) of 1-acetyl-2-benzylidene hydrazine in 50 ml. of absolute ethanol was shaken with 0.25 g. of palladium black catalyst under 50 p.s.i. of hydrogen at 25°. The reaction mixture was filtered and the filtrate evaporated to dryness, *in vacuo* at 25°, to give a residue, m.p. 78–81°. The residue was dissolved in 100 ml. of water, the solution acidified to *p*H 5 and extracted with four 100-ml. portions of ethyl ether. The ethereal extracts were combined, dried over anhydrous sodium sulfate, filtered, and the filtrate evaporated *in vacuo* to give a residue, m.p. 80–82° in 74% yield. This latter residue was recrystallized from anhydrous ethyl ether to give 43% of 1-acetyl-2-benzylhydrazine, m.p. 81–82°.

Anal. Calcd. for $C_9H_{12}N_2O$ (164): C, 65.8; H, 7.4; N, 17.1. Found: C, 65.9; H, 7.4; N, 16.9.

Infrared spectrum in chloroform: N—H, 3425 and 3289 cm.$^{-1}$; amide I, 1667 cm.$^{-1}$; amide II, 1548 cm.$^{-1}$; other prominent peaks, 1495, 1456, 1370, and 1277 cm.$^{-1}$

Initially the above reduction gave low melting products (70–80°) which could not be purified by recrystallization from ethyl ether. The impurity was found to be acethydrazide which has an amide II band at 1659 cm.$^{-1}$ This band was exhibited by all impure products. Acethydrazide can be removed from these products by dissolving them in water and extracting the aqueous solution, acidified to *p*H 5, with ethyl ether.

To 4.2 g. of 1-acetyl-2-benzylhydrazine in 30 ml. of triethylamine and 30 ml. of benzene was added 3.2 g. of redistilled phenyl isocyanate, the solution heated on a steam bath for 1 hr., cooled, the precipitate collected, washed with pentane, and recrystallized from chloroform to give 46% of 1-acetyl-2-benzyl-4-phenyl semicarbazide, m.p. 183.0–183.7°.

Anal.. Calcd. for $C_{16}H_{17}N_3O_2$ (283): C, 67.8; H, 6.0; N, 14.8. Found: C, 67.7; H, 6.2; N, 14.7.

To 104 g. (0.5 mole) of benzalazine in 400 ml. of absolute ethanol was added in the course of 2 hr. an amount of freshly prepared sodium amalgam equivalent to 1.05 moles of sodium,[16] the mixture stirred an additional 4 hr. at 25° and then poured into 3500 ml. of water. The precipitated benzalbenzylhydrazine[16] was collected, washed with cold water, and then taken up in 1 l. of boiling 1*N* hydrochloric acid. The acidic solution was filtered, the filtrate steam distilled, the residue from the steam distillation neutralized with calcium oxide, filtered, and the filtrate fractionally distilled to give 30 g. of benzylhydrazine, n_D^{25} 1.554. Acetylation of the benzylhydrazine with acetic anhydride gave 1-acetyl-2-benzylhydrazine identical with that described above.

Ethyl 1-acetyl-2-benzyl carbazate. To 16.4 g. (0.1 mole) of 1-acetyl-2-benzylhydrazine in 75 ml. of dry chloroform was added 10.2 g. of triethylamine, redistilled over sodium, and the solution cooled in an ice-salt bath. To the cold solution was added, in the course of 30 min., 10.9 g. (0.1 mole) of ethyl chloroformate in 25 ml. of dry chloroform, the reaction mixture maintained at 0° for an additional 30 min. and then at 25° for 16 hr. The chloroform solution was washed with 60 ml. of 2*N* hydrochloric acid, 60 ml. of saturated aqueous sodium bicarbonate, two 100-ml. portions of water, dried over anhydrous sodium sulfate, decolorized at 25° with Norite, filtered, and the filtrate evaporated *in vacuo* at 25° to give a viscous oil, which was transferred to a high vacuum system and degassed at 25° at a pressure below 10^{-4} mm. The final product, a viscous, colorless oil, n_D^{25} 1.5173, resisted all attempts at crystallization. The yield was 91%.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$ (236): C, 61.0; H, 6.8; N, 11.9. Found: C, 61.0; H, 7.0; N, 12.2.

Infrared spectrum in carbon tetrachloride: N—H stretch, 3268 cm.$^{-1}$; C=O stretch, 1718, 1689 cm.$^{-1}$; C=N stretch, absent; C—O—C stretch, absent; C—CH_3 C—H def. symm., 1379 cm.$^{-1}$; C—CH_3, C—H def. asymm., 1441 cm.$^{-1}$

(11) B. M. Iselin and C. Niemann, *J. Biol. Chem.*, **182**, 821 (1950).

(12) T. Curtius and T. S. Hoffman, *J. prakt. Chem.*, **53**, 513 (1896).

(13) T. Curtius and A. Burckhardt, *J. prakt. Chem.*, **58**, 205 (1898).

(14) T. Curtius, G. Schofer, and N. Schwan, *J. prakt. Chem.*, **51**, 185 (1895).

(15) R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921).

(16) A. Wohl and C. Oesterlin, *Ber.*, **33**, 2736 (1900)

Solubility: 0.05*M* in water, freely soluble in chloroform, carbon tetrachloride, acetone, and ethanol.

2-Methyl-4-benzyl-1,3,4-oxadiazolone-5. The attempted distillation of ethyl 1-acetyl-2-benzyl carbazate, at 0.1 mm. and a maximum bath temperature of 125°, gave 2-methyl-4-benzyl-1,3,4-oxadiazolone-5, a colorless oil, n_D^{25} 1.5335, d_4^{25} 1.192, and ethanol, the latter compound being collected in a Dry Ice trap.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$ (190): C, 63.2; H, 5.3; N, 14.7. Found: C, 63.4; H, 5.3; N, 14.5.

Infrared spectrum in carbon tetrachloride: N—H stretch, absent; C=O stretch, 1795 cm.$^{-1}$; C=N stretch, 1642 cm.$^{-1}$; C—O—C stretch, 1314 cm.$^{-1}$; C—CH_3 C—H def. symm., 1393 cm.$^{-1}$; C—CH_3 C—H def. asymm., 1437 cm.$^{-1}$. Solubility: 0.002*M* in water, freely soluble in chloroform, carbon tetrachloride, acetone, and ethanol.

Phosgene was passed into a boiling solution of 16.4 g. (0.1 mole) of 1-acetyl-2-benzylhydrazine in 200 ml. of chlorobenzene, concurrently with a stream of dry nitrogen. After 1 hr., when absorption of phosgene appeared to be complete, the solution was cooled to room temperature, washed with 100 ml. of 5% aqueous sodium bicarbonate and two 100-ml. portions of water, dried over anhydrous sodium sulfate, and fractionally distilled to give 82% of 2-methyl-4-benzyl-1,3,4-oxadiazolone-5, b.p. 0.025 mm. 112°, n_D^{25} 1.5337.

2-Methyl-1,3,4-oxadiazolone-5.[8] Phosgene was passed into a solution of 74 g. (1 mole) of acethydrazide in 500 ml. of water until an increase in weight of 75 g. had occurred. The reaction mixture was allowed to stand at room temperature for 2 days, neutralized with solid sodium bicarbonate, evaporated to dryness *in vacuo*, the residue transferred to a Soxhlet extractor, extracted with benzene, and the benzene extract cooled to give 25.2 g. (25%) of the desired product, m.p. 110–111.5°; lit.,[8] m.p. 112°.

Anal. Calcd. for $C_3H_4N_2O_2$ (100): C, 36.0; H, 4.0; N, 28.0. Found: C, 36.0; H, 4.2; N, 28.0.

2-Methyl-1,3,4-oxadiazolone is soluble in water and in this solvent is an acid of $pK_A' = 7.93 \pm 0.02$. Its solubility in carbon tetrachloride is limited but its solubility in chloroform is sufficient for determination of infrared spectra.

Infrared spectrum in chloroform: N—H stretch, 3472, 3268 cm.$^{-1}$; C=O stretch, 1786 cm.$^{-1}$; C=N stretch, 1650 cm.$^{-1}$; C—CH_3 C—H def. asymm., 1435 cm.$^{-1}$; C—CH_3 C—H def. symm., 1390 cm.$^{-1}$; C—O—C stretch, 1321 cm.$^{-1}$ and a very strong band that may be associated with an N—N stretch at 935 cm.$^{-1}$ [17-19]

N-Nitrosobenzylurethane. To 96.4 g. (0.9 mole) of redistilled benzylamine in 300 ml. of ethyl ether over 40 g. of sodium hydroxide in 200 ml. of water was added 97.5 g. ethyl chloroformate in 100 ml. of ether. The acid chloride was added in small portions to the vigorously shaken and cooled biphasic system. The ethereal phase was collected, dried over anhydrous sodium sulfate, the ether removed *in vacuo*, and the residue distilled at 17 mm. to give 75% of benzylurethane, m.p. 44°.[20] To a 1 l., three neck flask was added 33 g. (0.4 mole) of anhydrous sodium acetate and 250 ml. of carbon tetrachloride, the flask cooled in a powdered Dry Ice bath and 18.4 g. (0.2 mole) of nitrogen dioxide passed into the suspension. The mixture was brought to 0°, a solution of 24.1 g. (0.135 mole) of benzylurethane in 300 ml. of carbon tetrachloride added with stirring over a period of 20 min., the mixture poured over crushed ice and extracted with ethyl ether. The combined ether–carbon tetrachloride extract was washed once with 200 ml. of 10% aqueous sodium carbonate and twice with 200 ml. of water. The nonaqueous phase was dried over anhydrous sodium sulfate, the solvent removed *in vacuo*, at a temperature below 40°, and the residue degassed at 25° and 0.1 mm. to give the nitrosourethane as an amber colored liquid n_D^{25} 1.5166, d_4^{25} 1.1500, in 94% yield. *This product is a vesicant and must be handled with care.*

Infrared spectrum in carbon tetrachloride: N—H absent, a sharp increase in the intensity of the 1379 cm.$^{-1}$ peak, weak in benzylurethane, and a new strong band at 1348 cm.$^{-1}$, which may be due to the —N—N=O group.

Ultraviolet spectrum in 95% ethanol: λ_{max} = 247 mμ, ϵ = 11,600.

Reduction of N-nitrosobenzylurethane. *N*-Nitrosobenzylurethane, 41.6 g. (0.2 mole), 55.8 g. (0.85 g.-atom) of powdered zinc, 82 ml. of water and 85 ml. of glacial acetic acid (0.96 mole) was stirred at 10° for 20 min., 3.5 hr. at 25° and finally for 1 hr. on a steam bath. The reaction mixture was partitioned with 300 ml. of ethyl ether, filtered, the ethereal layer washed with 100 ml. of 10% aqueous sodium hydroxide, 100 ml. of water, dried over anhydrous sodium sulfate, the ether removed *in vacuo* and the residue distilled at 0.2 mm to give a product, b.p. 106°, n_D^{25} 1.5189 in 85% yield.

Anal. Calcd. for $C_{21}H_{25}N_3O_5$ (399): C, 63.2; H, 6.8; N, 10.5. Found: C, 63.6; H, 7.4; N, 10.7.

Infrared spectrum in carbon tetrachloride: N—H stretch, 3448, 3344 cm.$^{-1}$; C=O stretch, 1733, 1709 cm.$^{-1}$; amide II; 1515 cm.$^{-1}$; C—CH_3 C—H def. 1446, 1381 cm.$^{-1}$

Hydrolysis of the preceding product with concentrated hydrochloric acid gave benzylurethane and ethyl 2-benzyl carbazate obtained as an oil, b.p. 93–95° (0.5 mm.), n_D^{25} 1.5214 in 98% yield.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$ (194): C, 61.8; H, 7.3; N, 14.4. Found: C, 61.7; H, 7.2, N, 15.0.

Reaction of the oil with benzaldehyde gave ethyl 1-benzylidene-2-benzyl carbazate, m.p. 66–67°, lit.,[3] m.p. 64–65°.

Anal. Calcd. for $C_{17}H_{18}N_2O_2$ (282): C, 72.3; H, 6.4; N, 9.9. Found: C, 72.6; H, 6.5; N, 9.9.

Oxidation of the original product with alkaline permanganate gave benzoic acid and an unidentified aryl ketone, m.p. 145–146°.

All attempts to reduce *N*-nitrosobenzylurethane with hydrogen over palladium or platinum black led only to the isolation of benzylurethane.

Ethanolysis of 2-methyl-4-benzyl-1,3,4-oxadiazolone-5. To 3.98 g. of 2-methyl-4-benzyl-1,3,4-oxadiazolone-5 in 20 ml. of benzene was added 6 ml. of 0.5*N* ethanolic sodium ethoxide, the solution heated at its refluxing temperature for 30 min., cooled, successively washed with 10-ml. portions of 5% hydrochloric acid, 5% aqueous sodium bicarbonate and water, dried over anhydrous sodium sulfate, the solvent removed below 25°, and the residue degassed at 25° at a pressure below 10^{-4} mm. to give 3.8 g. of ethyl 1-acetyl-2-benzyl carbazate, a viscous oil, n_D^{25} 1.5216. The infrared spectrum of this product was identical with that obtained by treating 1-acetyl-2-benzylhydrazine with ethyl chloroformate. Degassing at 77° gave a product which contained a small amount of the starting material, as indicated by the presence of cyclic C=O absorption at 1795 cm.$^{-1}$

PASADENA, CALIF.

(17) D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman, *J. Am. Chem. Soc.*, 71, 2293 (1949).

(18) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1958.

(19) R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, 22, 204 (1957).

(20) S. Basterfield, E. L. Woods, and H. N. Wright, *J. Am. Chem. Soc.*, 48, 2371 (1926).