Synthesis of 2-Methylcarbamazepine, a New Internal Standard for Chromatographic Assays of Carbamazepine (Tegretol®)

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The synthesis of 2-methyl-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide (2-methylcarbamazepine, 2-MCBZ, **8**), a promising internal standard for chromatographic assays of the antiepileptic agent carbamazepine (CBZ, **1**), is described. *N*-(*p*-Tolyl)anthranilic acid (**2**) was utilized as a starting material for the synthesis of a key compound, 2,9-dimethylacridine (**4**), which was converted in two steps to 2-methyl-9-hydroxymethylacridan (**6**). The acridan **6**, in the presence of polyphosphoric acid, was ring-expanded to form 2-methyl-5*H*-dibenz[*b*,*f*]azepine (**7**), this latter compound being converted by conventional reactions to its 5-carbamyl derivative, 2-MCBZ (**8**).

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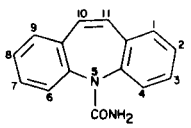
Introduction.

Carbamazepine (5*H*-dibenz[*b*,*f*]azepine-5-carboxamide, **1**), approved by the FDA in 1974, is indicated for treatment of complex partial and secondary generalized epilepsy (1,2) and for trigeminal neuralgia (3). The drug is widely used in epilepsy, being one of the five major antiepileptic agents (4). The development of more reliable chromatographic assays of carbamazepine (CBZ, **1**) presents one of the major challenges for programs involved in the routine monitoring of the antiepileptic agents (5). One of the principal causes of interlaboratory variability in antiepileptic drug assays has been the lack of appropriate internal standards for the analytical chromatographic methods (5, 6).



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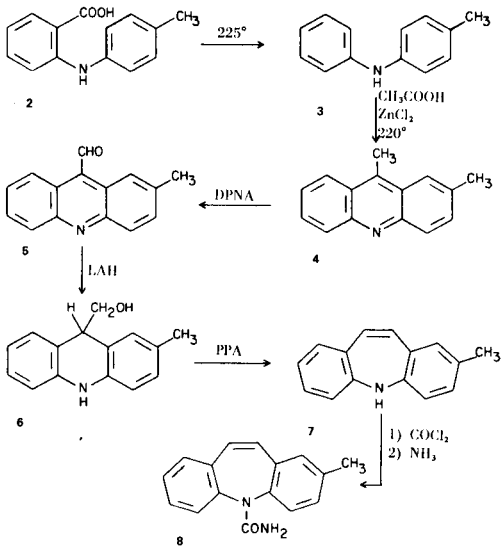
In the present study, the synthesis of 2-methylcarbamazepine (2-methyl-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide, **8**, 2-MCBZ), a promising candidate as an internal standard for CBZ assays, is described.

Results.

The reaction sequence employed for the synthesis of 2-methylcarbamazepine (**8**) is summarized in Scheme I.

Scheme I



The syntheses of *N*-(*p*-tolyl)anthranilic acid (**2**) and 4-methyldiphenylamine (**3**) were carried out by modifications of previous methods (7, 8). In the preparation of **2**, the addition of a small quantity of copper powder to the reaction mixture, as suggested by Ullmann and Bader (9) in 1907, facilitated the reaction, yields of **2** being in the neighborhood of 50 and 85% in the absence and presence of copper powders, respectively. Ullmann and Bader (9) also reported that **2** was converted to **3** in quantitative yield by thermal decarboxylation and distillation at 316°/704 mm, but in the present study this step was more conveniently carried out at 225° in the presence of cupric carbonate (10), despite a reduction of the yield to 50%. The yield of **3** was comparable to that obtained by other investigators (8) in their synthesis of an isomer of **3**. A fusion of the diphenylamine **3** in a glacial acetic acid-zinc chloride mixture at 230° afforded 2,9-dimethylacridine (**4**), with consistent recoveries of 50-60% being obtained.

The trace hydrochloric acid catalysis method of Tsuge, *et al.* (11) was employed to effect the condensation reaction between the 9-methyl substituent of **4** and *N*,*N*-dimethyl-*p*-nitrosoaniline (DPNA). This functionalization, as described by Tsuge, *et al.* (11), results in the formation of a mixture of products, an "anil" and a "nitrone," with the "anil" predominating in this particular example by a factor of about 22. In the present investigation, the "anil-nitrone" mixture was isolated without confirmation of composition and was converted directly to the aldehyde

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5, the overall conversion being about 55-60% in repeated trials. Tsuge, *et al.*, (11) also found that replacement of the trace quantity of hydrochloric acid by sodium carbonate, a reagent commonly used in this type of reaction, resulted in a greatly diminished yield in this specific reaction (**4** → **5**). In the present study, it was observed that piperidine, too, was less suitable as a catalyst, the general method of Varma, *et al.*, (12) providing inconsistent and lower yields and demanding extensive purification of product when applied to the conversion, **4** → **5**.

Lithium aluminum hydride reduction of the aldehyde **5**, when carried out under a nitrogen atmosphere, afforded a respectable yield (60-65%) of 2-methyl-9-hydroxymethylacridan (**6**). Even the crystalline form of **6** was extremely labile to autoxidation, decomposing within a day to a tar if precautions were not taken to protect the compound from air. As evidenced by the uv and visible spectral properties of **6**, when observed as a function of

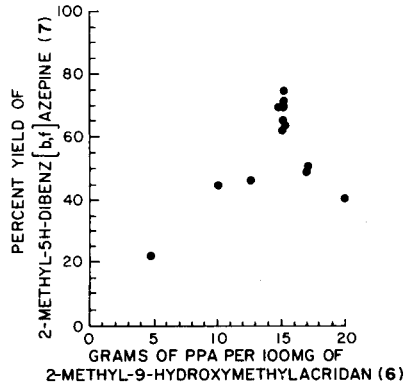


Figure 1. Effect of the quantity of polyphosphoric acid (PPA) on the ring expansion reaction of 2-methyl-9-hydroxymethylacridan (**6**).

Table I

Ultraviolet and Visible Light Absorption Data

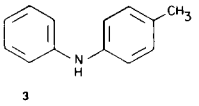
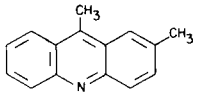
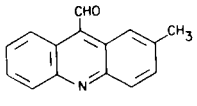
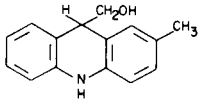
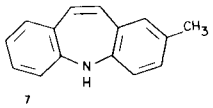
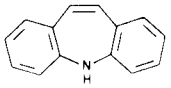
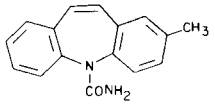
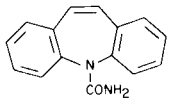
Compound	Solvent (a)	λ max	ε x 10^{-3}
 3	Ethanol	207	26.0
		287	20.7
 4	Ethanol	220	12.7
		250	187.5
		359	8.8
		383sh	3.9
	0.1*N* Hydrochloric acid	218	15.4
		262	113.9
		341	8.3
		358	17.5
		409	4.1
 5	Ethanol	230	24.5
		256	113.8
		362	8.5
	0.1*N* Hydrochloric acid	217	16.3
		263	99.2
		346	8.7
		362	17.6
		413	3.9
 6	Ethanol (b)	209	33.1
		285	15.9
	0.1*N* Hydrochloric acid (b)	209	33.0
		285	15.6

Table I continued

 7	Ethanol	211 261	24.3 43.5
 9	Ethanol	210 260	21.7 41.2
 8	Ethanol	216 240sh 287	32.9 16.0 11.7
 1	Ethanol	215 239sh 286	28.7 14.2 11.0

(a) Solutions were made by diluting stock ethanol solutions which ranged from 2 x 10^{-1} *M* to 7 x 10^{-3} *M*. Those solvents listed as 0.1 *N* hydrochloric acid were prepared by mixing 0.1 ml. of ethanol stock and 0.1 ml. of 0.1 *N* hydrochloric acid and by diluting this mixture to 10 ml. with ethanol.

(b) Values were calculated from spectra measured immediately after preparation of the solutions. When these solutions were allowed to stand at room temperature over a period of four days, the spectral changes were consistent with the conversion of the acridan system to an acridine system.

time, autoxidation of **6** results in reconstitution of the acridine ring system.

Ring expansion of the 9-hydroxymethylacridan **6** to form 2-methyl-5*H*-dibenz[*b*,*f*]azepine (**7**) was accomplished by use of polyphosphoric acid (PPA). As shown in Figure 1, the yield of the rearrangement product **7** was dependent upon the ratio of PPA to compound **6**, with an optimal yield of about 70% being obtained when approximately 15 g. of PPA per 100 mg. of **6** was employed. Craig, *et al.*, (13), in related studies of this rearrangement reaction, found that the use of phosphorous pentoxide in xylene was preferable to PPA, but their method, as applied to compound **6**, resulted in poor yields of **7** (~5%).

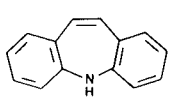
The final step entailed two sequential reactions, the conversion of 2-methyl-5*H*-dibenz[*b*,*f*]azepine (**7**) to its 5-carbamylchloride derivative (isolated in crude form) and an ammonolysis reaction of this 5-carbamylchloride derivative to form 2-MCBZ (**8**). Schindler (14) employed these same reactions in his synthesis of CBZ (**1**) from iminostilbene (5*H*-dibenz[b,f]azepine, **9**). However, the use of his ammonolysis procedure (14) presented much difficulty in the present study. For unexplained reasons, the employment of heat to facilitate the ammonolysis reaction caused an unidentified by-product to accompany the formation of **8**. Innumerable attempts were made to design chromatographic, solvent partitioning, and recrystallization techniques for removal of this impurity, all without evidence of success and gain of insight into the nature of the contaminant. The formation of this despicable contaminant was eliminated by initiating the ammonolysis reaction at 5-10° and by allowing it to proceed (closed steel bomb) at 25°. With this modification, the conversion of **7** to **8** was realized in 74% yield.

The ultraviolet and visible absorption data of the compounds in Scheme 1 and of some pertinent reference compounds are summarized in Table 1. The spectra of 2,9-dimethylacridine (**4**) and 2-methyl-9-acridinecarboxaldehyde (**5**) in ethanol and dilute acid solution were similar, but the two compounds could be distinguished qualitatively by the definitive 383 nm shoulder (ϵ, 3,900) exhibited by **4** in ethanol. The 9-hydroxymethylacridan **6** showed no absorption peaks above 285 nm, when spectra were recorded immediately after the preparation of its solutions. However, within time, absorption characteristic of the acridine structure developed in both solutions. After 4 days, the spectra indicated that autoxidation of the acridan system to form an acridine system was complete, but experimentation was not carried out to ascertain

whether the 9-hydroxymethyl substituent of **6** had been altered. The ultraviolet spectra of the 5*H*-dibenz[*b*,*f*]-azepine system was significantly different from those of the acridine and acridan precursors, as shown by comparison of the data of compounds **7** and **8** with those of compounds of **4**, **5** and **6**. The new 5*H*-dibenz[*b*,*f*]-azepines, **7** and **8**, had spectra identical with those of the reference compounds, iminostilbene (**9**) and CBZ (**1**), respectively.

Discussion.

The assay of CBZ (**1**), a unique antiepileptic agent from its structural standpoint, has presented much difficulty to the analytical chemist in applications of glc (15). CBZ (**1**) itself is thermally unstable in glc, decomposing in part to iminostilbene (**9**) (16-18). According to Frigerio, *et al.*, (17), this degradation of CBZ (**1**) to **9** is accompanied by the formation of 9-methylacridine (**10**), a rearrangement product isomeric with **9**. The variable manner in which CBZ (**1**) is converted by thermal processes to degradation and derivatization products in on-column methylation (19-22) and in silylation (23) procedures has furthermore complicated the analytical applications of glc.



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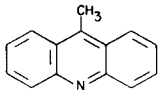

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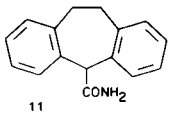

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In a glc assay, in which the analytic solute experiences non-reproducible pyrolytic, degradative, or derivatization reactions, the acquisition of reliable quantitative data becomes a demanding chore, unless the internal standard shares essentially the same chemical disposition as the drug itself (24). Several structurally different compounds have been used as internal standards in CBZ assays (18-20, 23, 25), one of the more popular being cyheptamide (10,11-dihydro-5*H*-dibenz[*a*,*d*]cycloheptene-5-carboxamide, **11**). However, these compounds, including **11**, are incapable of undergoing in proportional manners the pyrolytic, degradative, and on-column methylation derivatization reactions now recognized for CBZ (**1**) in glc. In the present investigation, the premise for the synthesis of a candidate internal standard like 2-MCBZ (**8**) was based upon empirical observations made in analytical studies of some other antiepileptic (24) and non-related drugs (26). In recent studies of some other antiepileptic agents, evidence has been obtained to show that the replacement of a phenyl substituent by a tolyl substituent results in a drug derivative which is an exceptional internal standard in glc. (27).

The structure of 2-MCBZ (**8**) was viewed as the most appropriate for the carbamazepine internal standard candidate. In the selection of 2-MCBZ (**8**), consideration was given to the shortcomings of the envisioned synthetic route (Scheme I) and to potential analytical problems that might surface if the final compound were to have the methyl substituent at the 4-position of the carbamazepine structure. In the plan of Scheme I, the adoption of *N*-(*p*-tolyl)anthranilic acid (**2**) as a starting material for the synthesis of 2-MCBZ (**8**) permitted unequivocal assignment of the ring-position of the methyl substituent at all stages of the synthesis; for example, when the decarboxylated derivative, 4-methyldiphenylamine (**3**), was "ring-closed" to 2,9-dimethylacridine (**4**) and, at the later stage, when the 9-hydroxymethylacridan **6** was "ring-expanded" to form the 5*H*-dibenz[*b*,*f*]azepine **7**. The use of *N*-(m-tolyl)anthranilic acid in this sequence would have required certification of the position of the methyl substituent in the isomer(s) formed in elaboration of the acridine system and, again, in the ring-expansion reaction. Although the use of *N*-(*o*-tolyl)anthranilic acid would not have presented the problem of positional isomers, the derived 4-methyl-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide was considered a less appropriate candidate, because of potential steric influence by the 4-methyl substituent on the reactivity and stability of the 5-carbamyl substituent.

Unpublished studies in our laboratory indicate that 2-MCBZ (**8**) is superior to cyheptamide (**11**) as an internal standard. In these preliminary studies, in which the design of the experiments challenges the behavior of CBZ (**1**) and 2-MCBZ (**8**) in the presence and absence of on-column methylating agent (0.3 M trimethyl phenylammonium hydroxide in methanol), the evidence shows that the degradation and derivatization products of **1** and **8** are formed to the same proportional extent. Although the analytical aspects of our present investigation are incomplete, we are confident that 2-MCBZ (**8**) is the most promising substance available at present as an internal standard for gas chromatographic assays of CBZ (**1**).

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 257 spectrophotometer; samples were prepared in the form of potassium bromide disks. Ultraviolet and visible spectra were measured on a Beckman Model 25 spectrophotometer in ethanol unless otherwise noted. Melting points were taken on a Kofler hot stage microscope and are corrected. Aluminum Oxide Woelm (neutral, activity grade I) was used for column chromatography. Thin layer chromatography (tlc) was carried out with microscope slides coated with Silica Gel H, a solution of 5% phosphomolybdic acid in ethanol being used to visualize chromatographic zones. Tlc was used to follow the progress of all reactions and to check purities of the compounds. Some useful solvent systems were chloroform:methanol (9:1), for compound **5**; benzene:dioxane:-acetic acid (100:50:3), for compound **4**; benzene, for compound **7**; and, benzene:ethyl acetate:acetic acid (7:3:1), for the other materials. Elemental analyses were performed by Micro-Tech of Skokie, Illinois.

N-(*p*-Tolyl)anthranilic Acid (**2**).

Several runs, with product yields of about 50%, were carried

out at 185° by the general method of Allen and McKee (7). The use of copper powder (8) increased the yield significantly. In a typical scaled reaction, *p*-toluidine (625 g., 5.83 moles), *o*-chlorobenzoic acid (230 g, 1.47 moles), potassium carbonate (230 g.), powdered cupric oxide (5.5 g.), and copper powder ("electrolytic dust," 1.5 g.), afforded 281 g. (84%) of **2**, m.p. 195-196°., lit. (9) m.p. 195°; ir cm^{-1}: 3340 (m), 3030 (m), 2920 (m), 2870 (m), 2650 (m), 2570 (m), 1660 (s), 1650 (s), 1580 (s), 1510 (s), 1500 (s), 1450 (m), 1420 (m), 1330 (m), 1260 (s), 1170 (m), 1050 (w), 910 (m), 850 (m), 790 (m), 760 (m), 710 (w).

4-Methyldiphenylamine (**3**).

In a typical run, a mixture of compound **2** (125 g., 0.55 mole) and powdered cupric carbonate (8.4 g.) was heated at 225° for 2.5 hours (10). After cooling, the product was dissolved in ether (250 ml.) and the insoluble inorganic material was filtered off. The etheral solution was washed with portions of 10% sodium carbonate solution (total volume, 300 ml.) and dried over anhydrous sodium sulfate. After removal of the ether, compound **3** was vacuum-distilled (135°/0.50 mm), whereafter recrystallization of **3** was accomplished by use of ligroine (boiling range, 90-120°), yield 52 g. (52%), m.p. 89°, lit. (28) m.p. 88-89°, ir cm^{-1}: 3410 (s), 3020 (m), 2920 (m), 1600 (s), 1510 (s), 1500 (s), 1310 (m), 1240 (w), 1180 (w), 880 (w), 810 (m), 750 (s), 700 (s).

2,9-Dimethylacridine (**4**).

Compound **4** was prepared by modification of the procedure of Tsuge, *et al.*, (11). The quantities used in a typical experiment were as follows: Compound **3** (8.2 g., 45 mmoles), zinc chloride (36 g.), and glacial acetic acid (9 ml.). A mixture was stirred at 220° for 6 hours, the melt was taken up in hot 10% sulfuric acid solution, and the aqueous solution was made strongly alkaline with concentrated ammonium hydroxide. This mixture, which contained **4** precipitated as an oil, was extracted with benzene (500 ml.), and the benzene solution was partitioned with 10% sulfuric acid solution (~250 ml.). The aqueous phase was collected, made strongly alkaline (conc ammonium hydroxide), and partitioned with benzene (500 ml.). The benzene solution was dried (anhydrous sodium sulfate) and evaporated under reduced pressure. The residue (8.5 g.) was reconstituted in a small volume of benzene and chromatographed on a column of neutral alumina (130 x 25 mm), with benzene being used as the eluent. The crude product (6.3 g.) was recrystallized from petroleum ether (30-60°) to give 5.2 g. (56%) of **4**, m.p. 88-90°, lit. (11) m.p. 89.5-90°; ir cm^{-1}: 3450 (w), 3040 (w), 2910 (w), 1560 (w), 1515 (w), 1150 (w), 820 (m), 750 (m).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.81; H, 6.34; N, 6.60.

2-Methyl-9-acridinecarboxaldehyde (**5**).

A mixture of 2,9-dimethylacridine (**4**) (9.2 g., 44 mmoles), *N*,*N*-dimethyl-*p*-nitrosoaniline (13.3 g., 89 mmoles), 12 *N* hydrochloric acid (0.38 ml.) and absolute ethanol (600 ml.) was heated under reflux for 3 hours. The reaction solution was let stand overnight at room temperature and the dark red crystalline deposit (11.3 g.) of the nitrone-anil mixture was filtered off and dried *in vacuo*. A solution of the product (11.3 g.) in 4 *N* hydrochloric acid (200 ml.) was heated on a hot water bath (94°) for 30 minutes, and the precipitated hydrochloride salt was filtered off and washed with one small portion of saturated sodium chloride solution, and, then, with three successive small portions of 2 *N* hydrochloric acid. The hydrochloride salt was dissolved in hot water (125 ml.), and this solution was treated with 20% sodium acetate solution until precipitation of the aldehyde was complete. The crude aldehyde was filtered off from the hot solution and recrystallized from absolute ethanol, yield, 5.5 g. (56%), m.p. 144-147°, lit. (11) m.p. 145°; ir cm^{-1}: 3450 (w), 1690 (m), 1520 (w), 1440 (w), 1150 (w), 1040 (w), 820 (w), 760 (m).

Anal. Clacd. for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.26; H, 4.89; N, 6.08.

2-Methyl-9-hydroxymethylacridan (**6**).

To a stirred suspension of 1.03 g. (27 mmoles) of lithium aluminum hydride (LAH) in 40 ml. of dry ether, in a flask equipped to maintain anhydrous conditions and an atmosphere of nitrogen, was added in portions a total of 2.0 g. (9 mmoles) of compound **5** over a period of 10 minutes. The solution was heated under reflux for 2.5 hours, and, after an additional quantity of LAH (0.3 g., 8 mmoles) had been added, heating under reflux was continued for another 30 minutes. Excess LAH was decomposed by the successive and slow addition of the following reagents: water (1.3 ml.), 15% sodium hydroxide (1.3 ml.), and water (3.0 ml.). The completion of the addition of these reagents required a period of 1.5 hours. The insoluble material was filtered off. The etheral filtrate was extracted with 400 ml. of dilute hydrochloric acid (2 drops of 12 N hydrochloric acid per 100 ml. of water). The ether phase was collected, dried (anhydrous sodium sulfate), and concentrated to an orange semisolid under reduced pressure. The residue was recrystallized from ethyl acetate-hexane mixture to give off-white crystalline **6** (1.3 g., 63%), m.p. 130-132°. The substance deteriorates rapidly (within 24 hours) in the presence of air. Samples were stored at -20° in a desiccator under nitrogen. The analytical sample, colorless crystals of m.p. 130-132°, was prepared by further recrystallization from ethyl acetate-hexane; ir cm^{-1}: 3400 (m), 3280 (w), 3030 (w), 2930 (w), 2870 (w), 1610 (w), 1510 (m), 1495 (m), 1485 (m), 1310 (w), (w), 1260 (w), 1060 (m), 820 (w), 760 (m).

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.79; H, 6.93; N, 5.93.

2-Methyl-5*H*-dibenz[*b*,*f*]azepine (**7**).

Polyphosphoric acid (77 g.), contained in a 25 x 125 mm tube, was prewarmed on a water bath (to aid mixing) and 0.5 g. (2 mmoles) of compound **6** was throughly mixed in. The tube was immersed in the water bath (100°) for 2 hours (occasional stirring) and the solution was poured over ice (200 g.). The yellow precipitate was filtered off, washed with water, and vacuum dried. The crude product was dissolved in benzene, the insoluble material was filtered off, and the solution was concentrated and applied to a chromatography column (neutral alumina, 85 x 9 mm, eluent: benzene). Fractions which contained **7** (homogeneous by tlc) were combined and evaporated, yield, 0.35 g. (76%), m.p. 158-160°. The purity of this material is adequate for the next step. The analytical sample, m.p. 159-162°, was prepared by recrystallization from cyclohexane. ir cm^{-1}: 3380 (s), 3030 (w), 2930 (w), 1610 (w), 1510 (m), 1480 (m), 1300 (w), 1260 (m), 1130 (m), 1110 (w), 940 (w), 900 (w), 820 (s), 810 (s), 770 (m), 750 (s), 730 (m), 700 (m), 680 (m).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.79; H, 6.38; N, 6.55.

2-Methyl-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide (2-MCBZ, **8**).

An apparatus for the handling of phosgene was constructed as described (29), with the exception that additional sodium hydroxide traps were included. Phosgene was bubbled through a solution of 3.47 g. (17 mmoles) of **7** in 120 ml. of benzene for 1 hour, and then the reaction apparatus was flushed with nitrogen for 2 days. The remaining benzene (75-100 ml.) was evaporated by direct impingement of a stream of nitrogen, without the aid of heat

(requires about 3-4 hours), to provide a light yellow oil. The oil was dissolved in 100 ml. of absolute ethanol, and this solution was chilled to 0-5° and was saturated with anhydrous ammonia. The cold ammonicale ethanolic mixture was transferred to a stainless steel bomb (glass liner), and the bomb was sealed and let stand at room temperature for 24 hours, after which the ethanol and ammonia were removed by impingement with nitrogen (25°). The off-white crystalline residue was triturated under 100 ml. of benzene, the solvent then being separated by suction filtration and saved for a separate workup. The insoluble material was partitioned between 500 ml. portions of water and benzene, the organic layer being removed, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. This furnished a viscous residue (homogeneous by tlc) which was crystallized by adding water (25 ml.) to its solution in ethanol (50 ml.) and by storing the mixture at -20°. Three crops of white crystalline **8**, which amounted to 2.79 g., m.p. 82-85°, were obtained.

The original benzene wash solution (100 ml.) furnished an additional 0.3 g. of **8**, m.p. 82-85°, after the residue from evaporation of the benzene had been chromatographed (neutral alumina, 25 x 50 mm column; eluent: ethyl acetate-benzene, 1:1) and recrystallized twice from aqueous ethanol. The total yield of **8** was 3.1 g. (74%), m.p. 82-85°. This product was extremely difficult to dry, even when the sample was kept in a vacuum over concentrated sulfuric acid. Acceptable analytical results (±0.30%) were obtained from one sample which had been dried for 4 days as described above. In this run, the sample (3.1 g.) was recrystallized from ethyl acetate-hexane mixture (1:2), by allowing the mixture to stand at 25° (a day) and then at 4° (for 2 days), yield, 2.5 g., m.p. 124-128°. This material gave an acceptable C, H, and N analysis (values shown below) and provided **8** of m.p. 81-85° when further recrystallized from ethanol-water mixture, ir cm^{-1}: 3500 (m), 3350 (m), 3300 (m), 3180 (m), 3030 (m), 2930 (w), 1680 (s), 1590 (s), 1490 (m), 1390 (m), 1310 (w), 1260 (w), 1250 (m), 1120 (w), 890 (w), 820 (w), 800 (m), 780 (m), 760 (m).

Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found C, 76.73; H, 5.65; N, 11.32.

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