tion of ammonia could be the acid–base reaction shown in eq 4 followed by a nucleophilic cleavage (eq 5).

$$CHCl_3 + NH_2NH_2 \longrightarrow \bar{C}Cl_3 + \overset{+}{N}H_3NH_2 \quad (4)$$

$$\overset{+}{N}H_3NH_2 + \bar{C}Cl_3 \longrightarrow NH_3 + CCl_3NH_2 \quad (5)$$

Because of its probable mode of formation and of the contaminating by-products which we have described here and because of other adaptable methods,[1] this method is not a recommended procedure for the preparation of pure protonated diazomethane.[21-24] It is competitive with others[5-7] for the preparation of deuteriodiazomethane since a sample approximately 92% deuterated was obtained when no solvent was used and all starting materials contained 99% of the maximum possible deuterium.

Although there is convincing evidence that diazomethane will explode alone,[2] the presence of previously unknown contaminants may make these mixtures more explosive[25,26] than pure diazomethane from other sources.[4] While we recognize and respect the explosive unpredicability of diazomethane, our experience[27] supports recent evidence[1d] that contrary to previous practice ground-glass apparatus can be used in its preparation without incident. As a result of this study, however, we do not claim to understand the reasons for the unpredictability of the decomposition of diazomethane.

Experimental Section

Infrared measurements were recorded as liquids or gases using a Beckman IR-10, Perkin-Elmer 421, or Perkin-Elmer 237 instrument. The gas chromatographic analysis were performed with a F & M Model 700 gas chromatograph using a flame ionization detector and a 10% diisodecylphthalate on a Chromosorb W column.

Caution: Proper precautions must be taken when working with diazomethane.[2]

Preparation of Diazomethane.—Variations of the procedure of Staudinger and Kupfer[9] were used throughout (see Table I). Ground-glass joints were used throughout.[1d] All gaseous products were collected in a liquid nitrogen trap.

Preparation of Deuteriodiazomethane.—Deuterated chloroform and hydrazine hydrate were purchased from Merck Sharp and Dohme of Canada, Ltd. Potassium hydroxide-*d* was prepared by adding clean potassium directly to D_2O in a dry box using a nitrogen atmosphere. It was then dried over P_2O_5 in a vacuum desiccator. The KOD and $D_2NND_2 \cdot D_2O$ were placed in the reaction flask, while in the dry box. Connection of the reaction flask to the generating assembly and the addition of $CDCl_3$ to a dropping funnel were accomplished while helium flushed out the entire apparatus to prevent exchange with atmospheric moisture. Procedure then followed that of Staudinger and Kupfer.[9] Deuterated diazomethane was collected in a liquid nitrogen cooled trap and was twice distilled under vacuum from −80 to −196°. Ethylene was removed by exposing the sample, maintained at −150° by an isopentane bath, to vacuum pumping for 30 min.

Proof of the Presence of Dichlorocarbene.—From a reaction of 28.0 g (0.50 mol) of potassium hydroxide and 16.9 ml (0.167 mol) of dried ($CaCl_2$) and freshly distilled cyclohexene in 122 ml of methanol with 13.4 ml (0.167 mol) of chloroform, 3 ml of a yellow oil identified by glpc analysis as 7,7-dichlorobicyclo[4.1.0]heptane[13] was obtained. Infrared comparison with a known sample[13] confirmed the glpc analysis.

Isolation of Chloroacetylene from the Dehydrohalogenation of 1,1-Dichloroethylene.—In a three-necked 100-ml flask fitted with a condenser, an additional funnel, and a nitrogen inlet, 4.0 g of potassium hydroxide in 5.6 ml of hydrazine were stirred by a magnetic stirrer and treated dropwise with 1.58 g of 1,1-dichloroethylene. During the addition, the temperature was kept at 5°; the system was swept with dry nitrogen; and all volatile products were collected in a Dry Ice–acetone trap. A noticeable reaction occurred as the solution became yellow and a precipitate formed. After the mixture had been stirred for 1.5 hr, the trap was closed to the system and opened to an evacuated ir cell which was connected through a ballast flask and a drying tube ($CaCl_2$). After the product was allowed to warm to room temperature, the pressure in the cell was 200 mm. The ir spectra clearly revealed the presence of chloroacetylene.

Experiments to Elucidate Ammonia Formation Mechanism. A.—To 15 ml of methyl alcohol was added 1.5 g of sodium and 2.5 ml of anhydrous hydrazine. The resulting solution was heated to 50° for 0.5 hr, and all gaseous products were collected in a liquid nitrogen trap. No ammonia was present by ir analysis.

B.—Approximately 2 g of anhydrous hydrazine and 5.5 g of chloroform were heated together at 50° for 40 min with all gases being trapped in a liquid nitrogen trap. All ir peaks were assigned to chloroform and ammonia with the latter being the minor component.

Registry No.—Diazomethane, 334-88-3; deuteriodiazomethane, 17510-78-0; hydrazine, 302-01-2; chloroform, 67-66-3.

Acknowledgment.—This work was partially supported by a NASA grant, NsG-381, for which we are grateful.

(21) It has been proposed[22,23] that diazomethane is formed with amino isocyanide as intermediate. For rearrangement to diazomethane, another probable intermediate would be isodiazomethane,[22] which explodes at temperatures lower than those of the reaction conditions used here.[24]

(22) I. T. Millar and H. D. Springall, ref 22, p 476.

(23) E. Muller, "Neuere Anschauungen Der Organischen Chemie," 2nd ed, Julius Springer, Berlin, Germany, 1957, pp 452–454.

(24) J. P. Anselme, *J. Chem. Ed.*, **43**, 596 (1966).

(25) (a) Impure CH_2N_2 is said[2a] to be especially dangerous and explodes even at low temperatures. (b) Chloroacetylene is reported to be sensitive to oxygen and is a treacherous explosive.[26]

(26) E. H. Huntress, "Organic Chlorine Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948, p 930.

(27) In the course of this and other work, stopcocks and ground-glass joints were freely used in the apparatus for generating and storing diazomethane. Relatively pure samples of the compound have been passed through medium-porosity, fritted-glass bubblers and chromatographic columns using ground fire-brick as a supporting material and over irregularly shaped KOH and silica gel. No explosions were observed in any of these experiments.

During preparation and manipulation of diazomethane, no explosions have occurred using this or other more conventional procedures.[4] In contrast, an explosion occurred with a spectroscopically pure sample of solid diazomethane following 3 days' storage in liquid nitrogen.

The Preparation of 2-(Substituted amino)-3-phenyl-3H-indol-3-ols

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Received May 17, 1968

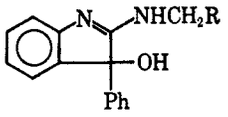
The synthesis of amidines from amides, without formation of intermediates such as imino chlorides or imidate salts, is known, but its preparative usefulness is limited to formamidines[1] or to special cases, such as the preparation of 2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]-pyrimidine from 1-(3-aminopropyl)-2-pyrrolidinone, where the amine function is held in proximity of the amide carbonyl.[2]

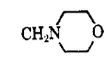
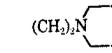
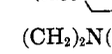
In the preparation of 1-methyl-2-(phenylimino)-pyrrolidine from 1-methyl-2-pyrrolidinone and aniline,

(1) J. B. Shoesmith and J. Haldane, *J. Chem. Soc.*, **123**, 2704 (1923).

(2) H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

TABLE I

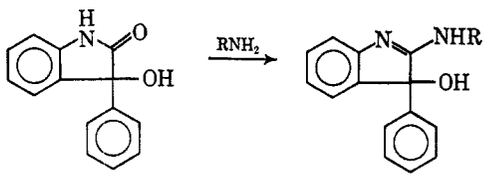


II	R	Mp, °C[a]	Yield, %[b]	Formula	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
a	Phenyl	156–157	32	$C_{21}H_{18}N_2O$	80.24	5.77	8.91	80.33	5.74	8.87
b	α-Pyridyl	219–221	71	$C_{20}H_{17}N_3O$	76.16	5.43	13.32	75.95	5.41	13.25
c	CH_2-α-Pyridyl	171–172	39	$C_{21}H_{19}N_3O$	76.58	5.82	12.76	76.45	5.86	12.84
d		187–189	55	$C_{20}H_{23}N_3O_2$	71.20	6.87	12.46	71.04	6.64	12.31
e	$(CH_2)_2N(CH_3)_2$	186–188	80	$C_{19}H_{23}N_3O$	73.74	7.49	13.58	73.55	7.47	13.73
f	$(CH_2)_2N(C_2H_5)_2$	164–165	60	$C_{21}H_{27}N_3O$	74.25	8.07	12.45	74.55	7.96	12.18
g		164–166	65	$C_{22}H_{27}N_3O$	75.45	7.79	12.03	75.15	7.70	12.00
h		157–158	70	$C_{21}H_{25}N_3O_2$	71.78	7.17	11.96	71.51	7.14	11.78
i	$(CH_2)_2N(C_2H_5)(CH)_2OH$	149–150	68	$C_{21}H_{27}N_3O_2$	71.37	7.70	11.90	71.14	7.70	12.01

[a] Melting points were observed on a Fisher-Johns block with a calibrated thermometer. [b] Solvent of recrystallization was 2-propanol.

phosphorus oxychloride is used,[3] and an imino chloride intermediate is first formed.

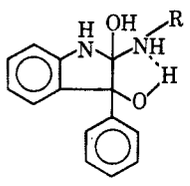
To our surprise, the preparation of the title compounds (II) was accomplished conveniently from 3-hydroxy-3-phenyloxindole (I), and an excess of primary amine in boiling xylene in the presence of a catalytic amount of *p*-toluenesulfonic acid by azeotropic removal of the water formed.



I II

The structure of II was established by infrared data. The oxindole carbonyl band at 1700–1715 cm^{-1} was missing. Instead, three bands at 1620, 1600, and 1580 cm^{-1} appeared, two assignable to phenyl ring vibrations, the remaining one due to C=N stretching vibration. As expected, in KBr the 3200-cm^{-1} region showed intermolecular bonded NH—OH, but in CCl_4 solution the free hydroxyl group was clearly visible at 3600 cm^{-1} and the NH group at 3440 cm^{-1}.

It was found that formation of amidine from I under the conditions used took place only when the 1 position was unsubstituted and free OH in the 3 position was present. It is known that the proton in the 3 position of I is quite readily removed. Hydrogen bridging from the 3-hydroxyl proton to the free electron pair in the addition product (III), necessary for the amidine formation, could block the amine nitrogen effectively, thus allowing protonation merely of the 2-hydroxyl group.



III

(3) H. Bredereck and K. Bredereck, *Chem. Ber.*, **94**, 2278 (1961).

Experimental Section

The preparation of the compounds in Table I is demonstrated in the following example.

2-[(3-Morpholinopropyl)amino]-3-phenyl-3H-indol-3-ol.—A mixture of 22.5 g (0.1 mol) of 3-hydroxy-3-phenyloxindole,[4] 28.8 g (0.2 mol) of 4-(3-aminopropyl)morpholine, and a catalytic amount of *p*-toluenesulfonic acid in 400 ml of xylene was boiled with stirring under a Dean–Stark trap for 10–15 hr, after which time 1.8 ml of water was collected. The solvent was evaporated under reduced pressure, and the residue was slurried in isopropyl ether, then recrystallized from 2-propanol to give 24.6 g (70%) of a white crystalline solid.

Registry No.—IIa, 17510-66-6; IIb, 17510-60-0; IIc, 17510-67-7; IId, 17510-61-1; IIe, 17510-62-2; IIf, 17510-63-3; IIg, 17510-64-4; IIh, 17510-65-5; IIi, 17510-59-7.

Acknowledgment.—The authors wish to thank Mr. C. E. Childs and staff for microanalytical data and Dr. J. M. Vandenbelt and Mr. E. J. Schoeb for infrared data.

(4) H. E. Baumgarten and P. L. Creger, *J. Amer. Chem. Soc.*, **82**, 4634 (1960).

Synthesis of β-Hydroxyamides from Phenylacetamides and Ketones or Aldehydes by Means of Alkali Amides and *n*-Butyllithium[1a]

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Received April 11, 1968

Until recently,[2] considerable difficulty was encountered in synthesizing β-hydroxyamide **2a** from

(1) (a) Supported at the University of Missouri by the Petroleum Research Fund, administered by the American Chemical Society, on Grant 959-G2, and at Duke University by the National Science Foundation; (b) University of Missouri; (c) Duke University.

(2) E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, **31**, 3316 (1966).