form was refluxed overnight while the condensate was passed through a Soxhlet extractor containing anhydrous sodium sulfate. The cupric sulfate was removed by filtration and the solvents were evaporated *in vacuo*. The residue was crystallized from ethyl acetate. Recrystallization from petroleum ether and from ethanol–water gave an analytical sample as yellow rods of m.p. 115–116°; λ_{max} 237 mμ (ε 20,000), 255 (sh) (17,000), 311 (6500), and 390 (5500).

Anal. Calcd. for $C_{17}H_{17}ClN_2O$: C, 67.88; H, 5.70. Found: C, 67.80; H, 5.67.

B. From 6-Chloro-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline 3-Oxide (II).—A suspension of 114.8 g. (0.4 mole) of 6-chloro-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline 3-oxide (II) in 3.5 l. of dry tetrahydrofuran was cooled to 5° with an ice bath, and 50 g. of potassium *t*-butoxide was added; the stirring and cooling were continued for 15 min. and then the mixture was filtered through Celite. The filtrate was concentrated *in vacuo*, and the residue was crystallized from hexane to give 53 g. (44%) of crude product, m.p. 105–108°. Recrystallization from ethanol–water and then from cyclohexane gave 37.5 g., m.p. 109–112°.

6-Chloro-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline (VII).—To a solution of 5 g. (17.4 mmoles) of II in 100 ml. of chloroform was added 2 ml. (23 mmoles) of phosphorus trichloride diluted with 20 ml. of chloroform. The mixture was heated under reflux for 30 min. and poured into 100 ml. of 1.2 *N* sodium hydroxide. The chloroform phase was separated, washed with 50 ml. of 10% sodium bicarbonate solution and 50 ml. of brine, and dried over sodium sulfate. This solution was filtered through 50 g. of alumina and the alumina was washed with 100 ml. of methylene chloride. The eluate was concentrated *in vacuo* and the residue was crystallized from hexane to give 2.5 g. (53%) of the product melting at 140–144°. An analytical sample, prepared by repeated crystallization from ethanol–water and from hexane–ether, formed yellow needles, m.p. 142–144.5°.

Anal. Calcd. for $C_{16}H_{15}ClN_2$: C, 70.60; H, 5.58. Found: C, 70.72, H, 5.89.

6-Chloro-1,2,3,4-tetrahydro-2,2-dimethyl-4-phenylquinazoline Hydrochloride (X). A. From 6-Chloro-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline (VII).—To a solution of 5 g. (18.5 mmoles) of VII in 400 ml. of methanol, cooled with an ice bath, was added 2.5 g. of sodium borohydride. The cold mixture was stirred for 6 hr., neutralized with acetic acid, and concentrated to dryness *in vacuo*. The residue was dissolved in 200 ml. of methylene chloride; the solution was washed with 100 ml. of water and dried over sodium sulfate. Concentration *in vacuo* left 5.34 g. of a pale yellow oil which had an infrared spectrum identical with that obtained in B. A solution of 2.73 g. of this oil in 10 ml. of methanol was treated with 1 ml. of 10 *N* methanolic hydrogen chloride and 80 ml. of ether. This procedure gave 1.9 g. of product, m.p. 220–240° dec.

B. From 2-Amino-5-chlorobenzhydrylamine (XI).[14]—A solution of 20 g. of 2-amino-5-chlorobenzhydrylamine (made from the corresponding dihydrochloride[15]) in 200 ml. of acetone containing 5 drops of glacial acetic acid was refluxed for 8 hr., and then it was evaporated *in vacuo*. The residue was extracted with hot hexane, which was filtered and evaporated to give 23 g. of an orange oil. This oil was dissolved in the calculated amount of 1 *N* methanolic hydrogen chloride and diluted with ether to give 24.2 (91%) of orange crystalline monohydrochloride, m.p. 225–230°. Additional crystallizations from methanol–acetone gave bright yellow rhombs, m.p. 230–243°.

Anal. Calcd. for $C_{16}H_{18}Cl_2N_2$: C, 62.14; H, 5.86; Cl, 22.93. Found: C, 62.09; H, 5.88; Cl, 22.73.

6-Chloro-1,2-dihydro-2-methyl-4-phenylquinazoline 3-Oxide (IV).—A solution of 50 g. of crude 2-amino-5-chlorobenzophenone *anti*-oxime[16] in 250 ml. of methanol was cooled with an ice bath to 5°. To this solution was added 5 ml. of acetic acid and 20 ml. of acetaldehyde (exothermic reaction). The mixture was filtered after standing in the ice bath for 1 hr. The precipitate was collected and recrystallized from isopropyl alcohol–water to give 16.6 g. (30%) of product, m.p. 170–174°. An analytical sample prepared by three recrystallizations from isopropyl alcohol formed yellow needles and melted at 174–176°.

Anal. Calcd. for $C_{15}H_{13}ClN_2O$: C, 66.05; H, 4.80. Found: C, 66.42; H, 4.98.

(14) This experiment was performed by Dr. G. A. Archer.

(15) S. C. Bell and S. J. Childress, *J. Org. Chem.*, **27**, 1961 (1962).

6-Chloro-2-methyl-4-phenylquinazoline 3-Oxide (VIII).—To a solution of 0.36 g. (1.2 mmoles) of sodium dichromate dihydrate in 10 ml. of acetic acid was added 1 g. (3.66 mmoles) of the dihydroquinazoline IV. The solution, which turned green immediately, was diluted in 100 ml. of methylene chloride and filtered through 25 g. of alumina. The residue, obtained after evaporation of the methylene chloride, was crystallized from ether–petroleum ether to yield 0.65 g. (60%) of VIII, m.p. 154–156° (sintering at 145°).[2a]

Attempted Reaction of Acetone Oxime with 2-Amino-5-chlorobenzophenone.—A solution of 10 g. (43.2 mmoles) of 2-amino-5-chlorobenzophenone and 5 g. of acetone oxime in 100 ml. of acetone and 0.5 ml. of acetic acid was heated under reflux for 3.5 hr. Thin layer chromatography of the reaction mixture on silica gel G plates developed with 5% methanol in chloroform indicated that no dihydroquinazoline (II) was present.

Hydrolysis of 6-Chloro-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline 3-Oxide (II) to 2-Amino-5-chlorobenzophenone *anti*-oxime (III).—A suspension of 10 g. of II in 100 ml. of 3 *N* hydrochloric acid was stirred at room temperature for 2 hr. The white solid was separated by filtration and resuspended in 100 ml. of water. This suspension was neutralized with solid sodium carbonate and filtered. The solid was washed with 100 ml. of water and recrystallized from benzene to give 6.9 g. (80%) of crude 2-amino-5-chlorobenzophenone *anti*-oxime, m.p. 120–129°. A solution of 2 g. of the crude oxime in 100 ml. of ether was washed with 50 ml. of 10% sodium bicarbonate solution, dried over sodium sulfate, and concentrated *in vacuo*. The residue was crystallized from benzene to give 1.3 g. of pure III, m.p. 129–132.5°. This product was identical with the *anti*- (β-) oxime described in the literature.[2a] By this process, 1,2-dihydro-2,2-dimethyl-4-phenylquinazoline 3-oxide gave a 53% yield of 2-aminobenzophenone *anti*-oxime[16] and 6-trifluoromethyl-1,2-dihydro-2,2-dimethyl-4-phenylquinazoline 3-oxide gave a 40% yield of 2-amino-5-trifluoromethylbenzophenone *anti*-oxime.[4]

2-Amino-5-nitrobenzophenone *anti*-Oxime from 1,2-Dihydro-2,2-dimethyl-6-nitro-4-phenylquinazoline 3-Oxide.—To a solution of 5.0 g. of 1,2-dihydro-2,2-dimethyl-6-nitro-4-phenylquinazoline 3-oxide in 100 ml. of boiling ethanol was added 2 ml. of concentrated hydrochloric acid, the mixture was refluxed for 5 min., and 100 ml. of cold water was added. After the mixture had stood for *ca.* 30 min., the precipitate was collected and washed with 50 ml. of water in two portions. Recrystallization from aqueous ethanol gave 2.3 g. (53%) of product, m.p. 200–203° (depressed on admixture of the *syn* isomer). After recrystallization from ethanol the oxime formed orange prisms, m.p. 197–203° dec.[2c]

Anal. Calcd. for $C_{13}H_{11}N_3O_3$: C, 60.72; H, 4.28. Found: C, 61.04; H, 4.27.

Acknowledgment.—We thank Dr. A. Steyermark, Mr. S. Traiman, Dr. V. Toome, and Dr. E. Billeter, respectively, for the microanalyses, the infrared spectra, the ultraviolet spectra, and the n.m.r. spectra. We also thank Mr. T. Flynn and Mr. R. DiMaio for their skillful technical assistance.

(16) K. v. Auwers and F. v. Meyerburg, *Ber.*, **24**, 2303, 2305, 2370 (1891).

Alkylation of Benzophenone with Aminoalkyl Halides in Liquid Ammonia

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Received May 24, 1965

Schlenk and Weikel[1] showed in 1911 that benzophenone forms a disodio derivative in ether and that

(1) W. Schlenk and T. Weikel, *Chem. Ber.*, **44**, 1182 (1911).

TABLE I
TERTIARY AMINO ALCOHOL HYDROCHLORIDES

$(C_6H_5)_2$—C(OH)—R·HCl

R	Yield, %	M.p.,[a] °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
$CH_2CH_2CH_2N$⟨ring⟩	51	223–224[b]	$C_{21}H_{28}ClNO$	72.92	8.16	4.05	72.75	8.15	4.33
$CH_2CH_2CH_2N(CH_3)_2$	55	204–206[c]	$C_{18}H_{24}ClNO$	70.69	7.91	4.58	70.64	8.05	4.64
$CH_2CH_2CH_2N$⟨ring⟩$N-CH_3$	60	143–144[d]	$C_{21}H_{28}N_2O$	77.74	8.69	8.63	77.60	8.45	8.50
$CH_2CH_2N(C_2H_5)_2$	53	202–204[e]	$C_{19}H_{26}ClNO$	71.43	8.19	4.38	71.46	8.08	4.69

[a] Melting points are corrected. [b] A. Marxer [*Helv. Chim. Acta*, **24**, 209E (1941)] reports m.p. 212–214°. [c] W. J. Croxall and J. W. Dawson [U. S. Patent 2,584,429] report m.p. 122–123.5° for the base. A sample of base obtained from hydrochloride salt had m.p. 121–123°. [d] Analyzed as the free base. A sample converted to the hydrochloride salt had m.p. 233–234°. H. E. Zaugg, R. J. Michaels, H. J. Glenn, L. R. Swett, M. Freifelder, G. R. Stone, and A. W. Weston [*J. Am. Chem. Soc.*, **80**, 2763 (1958)] report m.p. 232–233°. [e] D. W. Adamson [British Patents 624,118, 627,139 (1949)] reports m.p. 202–203°.

it can be alkylated with methyl iodide to give diphenylmethylcarbinol. In 1928, Wooster[2] showed that although this alkylation proceeded very slowly in benzene or ether, the reaction occurred very rapidly in liquid ammonia and a good yield of the desired product could be obtained. He was unsuccessful in his attempts to extend the reaction to aryl halides. Although it was not recognized at the time, Frey[3] had accomplished such an alkylation when he isolated triphenylcarbinol from his attempt to prepare benzophenone by the reaction of bromobenzene with diethyl oxalate and sodium. This product undoubtedly arose from the reaction of bromobenzene with the disodio derivative of benzophenone.

More recently Hamrick and Hauser[4] prepared the disodio derivative of benzophenone in liquid ammonia and reacted it with benzyl chloride and benzhydryl chloride to give 1,1,2-triphenylethanol and 1,1,2,2-tetraphenylethanol, respectively, in good yield.

The benzophenone disodio derivative has recently[5] been utilized for the preparation of cyclic ethers by the following reactions.

$$Ph_2C(Na)ONa + (CH_2)_nX_2 \longrightarrow Ph_2C\begin{matrix}O\\|\\(CH_2)_n\end{matrix}O + 2NaX$$

$n = 1, 2, 3, 4$

We have found that alkylation of the disodio derivative of benzophenone with aminoalkyl halides provides a convenient method for preparing a variety of amino alcohols, many of which are obtained in low yields by other procedures. The synthesis is outlined below.

$$Ph_2C{=}O \xrightarrow[2Na]{NH_3} Ph_2C(Na)ONa + RCl \xrightarrow[H_2O]{} Ph_2C(R)OH$$

The yields and properties of compounds which we have prepared by this procedure are shown in Table I.

(2) C. B. Wooster, *J. Am. Chem. Soc.*, **50**, 1388 (1928).
(3) H. Frey, *Chem. Ber.*, **28**, 2514 (1895).
(4) P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 493 (1959).
(5) D. V. Ioffe, *Zh. Obshch. Khim.*, **34**, 3900 (1964).

Experimental Section

General Procedure.—To approximately 2000 ml. of liquid ammonia cooled in a Dry Ice–isopropyl alcohol bath was added with stirring during 15 min. 48 g. (2 g.-atoms) of sodium. After 45 min. a solution of 182 g. (1.0 mole) of benzophenone in 500 ml. of ether was added during 30 min. After an additional 45 min., a solution of 1 mole of the aminoalkyl chloride in 500 ml. of ether was slowly added. The mixture was stirred for 1 hr., during which time it went from blue-black to pea green. Next the ammonia was evaporated with the aid of a water bath, and then 750 ml. of water was added while a nitrogen atmosphere was maintained. The reaction mixture set to a solid cake and 1000 ml. of benzene was added to facilitate stirring. Two clear layers formed and the organic phase was separated, washed three times with water, and dried. The dry solution was acidified with isopropyl alcohol containing 10% hydrogen chloride; the amino alcohol hydrochloride was separated by filtration. The crude product was obtained in yields of 70–90% and was purified by recrystallization from isopropyl or ethyl alcohol.

The Synthesis of 2,1,3-Benzothiadiazine 2,2-Dioxides and 1,2,3-Benzoxathiazine 2,2-Dioxides

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Received June 4, 1965

As a continuation of work underway in these laboratories[1] on the preparation of new heterocyclic systems based on sulfamide[2] as a starting material, we have investigated the reaction of sulfamide with *o*-aminobenzophenones and *o*-aminoacetophenones. We have found that simply fusing the amino ketones I with an excess of sulfamide at about 140° followed by heating at 180–190° affords good yields of 1H-2,1,3-benzothiadiazine 2,2-dioxides (II), a previously unreported heterocyclic system.[3]

(1) J. B. Wright, *J. Org. Chem.*, **29**, 1905 (1964).
(2) Obtained from General Chemical Division, Allied Chemical Corp.
(3) 1H-2,1,3-Benzothiadiazin-4-(3H)-one 2,2-dioxides have been reported recently: J. R. Geigy A-G., German Patent 1,120,456 (1962); E. Cohen and B. Klarberg, *J. Am. Chem. Soc.*, **84**, 1994 (1962).