




TABLE I
N,N-Bis(CYANOMETHYL)CARBOXAMIC ACIDS: HO₂C—(G)—CON(CH₂CN)₂

(G)	Formula	Yield, %	M.P., ² °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
—CH=CH—	C ₈ H ₇ N ₃ O ₃	70	132–5	49.70	49.74	3.63	3.81	21.80	21.95
—CH=CCl—	C ₈ H ₆ ClN ₃ O ₃	80	139–42	42.21	42.59	2.64	3.0	18.45	18.42
—CH(C ₆ H ₁₅)CH ₂ —	C ₁₆ H ₂₃ N ₃ O ₃	95	Part. solid	63.0	61.8	7.54	7.60	13.76	12.34
	C ₁₂ H ₁₃ N ₃ O ₃	70	147–9	58.3	58.0	5.26	5.50	17.0	16.6
	C ₁₃ H ₁₃ N ₃ O ₃	68	128–32	60.2	60.4	5.02	5.26	16.2	16.18
	C ₁₂ H ₉ N ₃ O ₃	90	168–70	59.2	59.2	3.71	3.90	17.3	17.54

Physical properties, analyses and yields of the products are given in Table I.

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(2) All temperatures are uncorrected.

Preparation of Phenyl diazomethane^{1,2}

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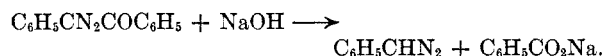
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Phenyl diazomethane has been prepared previously either by the action of concentrated aqueous base on the *N*-nitroso derivatives of benzylurethan,⁴ benzylurea,⁵ or benzylnitroguanidine,⁶ or by the oxidation of benzaldehyde hydrazone with mercuric oxide.⁷ Gutsche and Jason⁸ have recently compared these methods and concluded that the oxidative method was preferable. However, this method gave only an 80% yield (based on benzaldehyde) of crude phenyl diazomethane of ca. 40% purity.

As a result of our studies on the reaction of diazoketones with base⁹ we have developed a novel and convenient method for the preparation of phenyl diazomethane in ethereal solution from azibenzil in ca. 70% yield. The azibenzil in ethereal

solution was treated with an aqueous-methanolic solution of eight molar equivalents of sodium hydroxide; by suitable choice of the relative proportions of the three solvents a homogeneous solution was obtained which deposited only a trace of solid material during the course of the reaction. The solution was left to stand for eight hours at room temperature and then diluted with aqueous sodium hydroxide; the ethereal phenyl diazomethane layer was separated, washed, and dried. The identity and yield of the product were determined by reaction with *p*-nitrobenzoic acid and mandelic acid, which gave benzyl *p*-nitrobenzoate and benzyl mandelate in yields of 71 and 70%, respectively. Since azibenzil is readily prepared in high yield from benzil monohydrazone¹⁰ and, when pure, may be stored in the cold for several months without deterioration, this is an attractive method for the preparation of ethereal phenyl diazomethane.

Acidification of the aqueous basic layer gave a mixture of benzoic acid (90%) and diphenylacetic acid (6%). Thus *under these conditions* the major path of reaction may be formulated as:



This mode of cleavage of an aliphatic diazo compound has previously been suggested by Wilds and Meader¹¹ to account for the formation of *p*-chlorobenzoic acid from the action of warm aqueous-methanolic potassium hydroxide on *p*-chlorophenyl-*a*-diazopropiophenone; in this case, the other fragment was not identified.

A preliminary attempt was made to extend this method to the preparation of *p*-chlorophenyl diazomethane from 4,4'-dichloroazibenzil. However, although *p*-chlorobenzoic acid was obtained in high yield, the major neutral product was *p*-chlorobenzyl alcohol; this presumably arises from further reaction of the *p*-chlorophenyl diazomethane with the aqueous basic medium, the reaction being favored

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- (2) Work supported by an institutional research grant from the American Cancer Society to Harvard University.
- (3) Shell Foundation Fellow, 1955–1956.
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in this case by the presence of an electron-withdrawing substituent on the phenyl ring.

EXPERIMENTAL¹²

Azibenzil. Azibenzil was prepared from benzil monohydrazone¹³ by the method of Nenitzescu and Solomonica¹⁰ with the following minor modifications: (i) the reaction mixture was cooled slightly before addition of the cold, alcoholic potassium hydroxide in order to minimize the frothing which accompanies the initial reaction; (ii) the crude azibenzil was dissolved in ether at room temperature and the solution was allowed to stand at room temperature for 1–2 hours, decanted from traces of mercury which otherwise always contaminated the product, and cooled at -20° overnight to effect crystallization. Pure azibenzil remained unchanged after storage at 0° in a dark, evacuated desiccator for several months.

Phenyldiazomethane. A solution of sodium hydroxide (8 g., 0.2 mole) in a mixture of water (15 ml.) and methanol (100 ml.) was added to a solution of azibenzil (5.56 g., 0.025 mole) in ether (125 ml.). The container was loosely stoppered and the mixture was allowed to stand at room temperature for 8 hr. Occasionally a small amount of white solid, possibly sodium benzoate, came out of solution early in the reaction, but homogeneity was restored by addition of small amounts of alcohol and/or water.¹⁴ At the end of the reaction time a very small amount of pale yellow solid had been deposited (probably benzilazine⁹); this was removed by filtration and the clear, red solution was treated with 10% aqueous sodium hydroxide (100 ml.). The ethereal layer was washed with 10% aqueous sodium hydroxide (four 25-ml. portions) and dried over sodium sulfate, $\lambda_{\text{max}}^{\text{CCl}_4}$ 4.91 μ .

This ethereal solution of phenyldiazomethane was treated with *p*-nitrobenzoic acid in small amounts at a time until the solution was very pale yellow and further additions no longer caused gas evolution. The solution was washed with 5% aqueous sodium bicarbonate and with water, dried, and evaporated *in vacuo* to give benzyl *p*-nitrobenzoate (4.27 g., corresponding to a 71% yield of phenyldiazomethane); the infrared spectrum of the crude product showed only the bands of benzyl *p*-nitrobenzoate and one recrystallization from 95% ethanol gave the ester as shining plates, m.p. $82-82.5^{\circ}$ (rec.¹⁵ m.p. $83.5-84.5^{\circ}$) undepressed on admixture with an authentic sample. In another run, mandelic acid was used in a similar manner giving a yield of benzyl mandelate corresponding to a 70% yield of phenyldiazomethane; one recrystallization from ethanol gave material, m.p. $92.5-93.5^{\circ}$ (rec.¹⁶ m.p. 93°).

The aqueous basic layer and washings from the cleavage reaction were combined, cooled to 0° , acidified with dilute sulfuric acid, and extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated *in vacuo* to give a dirty white solid (3.00 g.). An aliquot of the solid was sublimed for 8 hr. at a bath temperature of 60° and a pressure of 0.5 mm. to give a sublimate of benzoic acid and a residue of diphenylacetic acid, each identified by its infrared spectrum, m.p., and mixed m.p. The yields of benzoic and diphenylacetic acid were 90 and 6%, respectively.

4,4'-Dichlorobenzil monohydrazone. A solution of 95+ % hydrazine (3.5 g., 0.1 mole) in absolute ethanol (20 ml.) was added to a stirred, refluxing suspension of 4,4'-dichloro-

benzil¹⁷ (27.9 g.: 0.1 mole) in absolute ethanol (650 ml.). With the addition of the hydrazine, the ketone went into solution. The solution was refluxed for 30 min. and then distilled with continuous slow addition of water until approximately 350 ml. of distillate had been collected; the hydrazone began to separate after the removal of about 200 ml. of ethanol. The mixture was cooled in an ice bath and filtered: the hydrazone was washed with water and dried to constant weight *in vacuo* at 80° ; yield, 28.1 g. (96%), m.p. $143-147^{\circ}$ dec. Five crystallizations from absolute ethanol gave the hydrazone as fluffy, white crystals, m.p. $149.5-151.5^{\circ}$ dec., $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 2.92, 3.05, 6.08 μ .

Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OCl}_2$: C, 57.36; H, 3.44; N, 9.56. Found: C, 57.60; H, 3.36; N, 9.68.

4,4'-Dichloroazibenzil. A suspension of 4,4'-dichlorobenzil monohydrazone (11.73 g., 0.04 mole), yellow mercuric oxide (30 g.: 0.14 mole) and anhydrous sodium sulfate (10 g.) in ether (150 ml.) was cooled to ca. 10° and treated with a few drops of cold, saturated ethanolic potassium hydroxide. A dark precipitate of mercury and mercury salts began to form immediately and the solution became dark orange-red. The suspension was shaken for 45 min. and then allowed to settle. The ethereal solution was decanted and the residual sludge was washed with ether by decantation until the washings were no longer colored. The combined solution and washings were allowed to stand for ca. 2 hr. to permit further separation of finely divided mercury, filtered, dried, and evaporated to a volume of about 100 ml. The solution was cooled at 0° overnight to give the diazoketone as shiny, orange spikes, m.p. $77-80^{\circ}$ dec.; yield, 6.31 g. (54%); a small additional yield could be obtained by concentration of the mother liquors. Five recrystallizations from ether gave material, m.p. $91-92^{\circ}$ dec., $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 4.85, 6.14, 7.47 μ .

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{OCl}_2$: C, 57.75; H, 2.77; N, 9.63. Found: C, 57.57; H, 2.82; N, 9.69.

Basic cleavage of 4,4'-dichloroazibenzil. The reaction of 4,4'-dichloroazibenzil with sodium hydroxide in ethereal-aqueous-methanolic solution was carried out exactly in the fashion used for the basic cleavage of azibenzil. Treatment of the orange-red, ethereal solution of the neutral product with benzoic acid and a few drops of boron trifluoride etherate gave a poor yield (ca. 50%) of a mixture of *p*-chlorobenzyl alcohol and *p*-chlorobenzyl benzoate (identified on the basis of the infrared spectrum). Acidification of the aqueous basic solution gave a 91% yield of *p*-chlorobenzoic acid, identified by infrared spectrum, m.p., and mixed m.p.

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Some Polyaryl Derivatives of Metals and Metalloids as Liquid Scintillator Solutes

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F. NEWTON HAYES

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In previous surveys¹ of compounds screened as liquid scintillator solutes, an attempt has been made

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