under a straight-edged object adjusted to give a coating about 0.5 mm. thick. It was found advantageous to dry the chromatostrips at 105° for 30 min. and to store them over potassium hydroxide in a desiccator until used.

For chromatography, a small spot of the solution to be developed was placed one centimeter above one end of a strip. The strip was immersed in the appropriate developing solution contained in a test tube. About 1.5 ml. of solvent in the tube is sufficient for development. Three solvent mixtures that we have found to be particularly useful are ether–Skellysolve B (7:3); ethyl acetate–Skellysolve B (3:1); and acetone–Skellysolve B (1:3).[9a]

For following the methylation of β-resorcylic acid, the ether: Skellysolve B (7:3) mixture was employed as the developer. The methoxy derivatives were observed on the strip as dark absorption spots when viewed under an ultraviolet lamp having a peak emission wave length at 2540 Å. At 15-min. intervals, samples were removed from the reaction mixture by means of a micropipet, acidified, and chromatographed. In this way, formation of the new methoxy compound and the disappearance of the reactant were simultaneously observed.

Methyl 2,4-dihydroxybenzoate. To 10 g. of β-resorcylic acid dissolved in acetone was added 10 g. of sodium carbonate, and while the mixture was boiling on a steam bath dimethyl sulfate and 10% methanolic potassium hydroxide were alternately added dropwise to maintain the *p*H at 7–8. The original spot representing β-resorcylic acid (R_f = 0.57) gradually changed during 1.5 hr. to a faster-moving spot (R_f = 0.73). After acidification of the reaction mixture and removal of acetone, the compound was extracted from the mixture with ether and crystallized from methanol to give colorless needles, producing a positive ferric chloride reaction, m.p. 117°.[9b] Hydrolysis of this compound with 10% methanolic potassium hydroxide for 0.5 hr. on the steam bath gave the original β-resorcylic acid. Therefore, the first product formed was the methyl 2,4-dihydroxybenzoate.

Anal. Calcd. for $C_8H_8O_4$: C, 57.1; H, 4.77; OMe, 18.4. Found: C, 57.1; H, 4.85; OMe, 18.4.

Rangaswami[9] described the preparation of the methyl-β-resorcylate by means of methanol and hydrochloric acid. The completely dried compound melted at 119°.

Methyl 2-hydroxy-4-methoxybenzoate. Continued heating of the solution of methyl ester and maintenance of the *p*H at 7–8 for 2.5 additional hours produced another compound which gave a single spot (R_f = 0.86). This material crystallized in the refrigerator from methanol and water as white needles, m.p. 46°. Mauthner[10] gave 48° as the melting point for this compound. The compound was the methyl 2-hydroxy-4-methoxy-benzoate.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.3; H, 5.49; OMe, 34.1. Found: C, 59.4; H, 5.62; OMe, 33.8.

2-Hydroxy-4-methoxybenzoic acid. Saponification of the acetone solution of methyl 2-hydroxy-4-methoxybenzoate for 4 hr. on the steam bath with 10% methanolic potassium hydroxide resulted in another pure compound as shown by a single blue fluorescent spot (R_f = 0.67). The isolated material, after removal of acetone and extraction into ether, was crystallized from methanol as colorless needles, m.p. 158°. The compound gave a positive ferric chloride test and was soluble in 5% sodium carbonate solution.

Calcd. for $C_8H_8O_4$: C, 57.1; H, 4.77; OMe, 18.4. Found: C, 57.1; H, 4.77; OMe, 18.8.

Mauthner[10] indicated158° as the melting point for 2-hydroxy-4-methoxybenzoic acid.

Methyl 2,4-dimethoxybenzoate. The methyl dimethoxybenzoate was conveniently formed by the alternate additions of dimethyl sulfate and 10% potassium hydroxide to a boiling acetone solution of β-resorcylic acid so as to maintain the *p*H at 11–12. The reaction went *via* the same methyl ester intermediates described above, but at the higher *p*H, the reaction was completed within 2 hr. and the chromatostrip showed only a single spot (R_f = 0.63). The material isolated was an amber-colored liquid at room temperature. It was further purified to a colorless liquid by distillation at 120° and 0.75 mm. It boiled at 293–296° under atmospheric pressure. No ferric chloride reaction was observed and the compound was not extracted from ether by 5% sodium carbonate.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.12; OMe, 47.5. Found: C, 60.9; H, 6.44; OMe, 45.0.

Perkin and Schiess[11] had previously described the preparation of this compound with a boiling point of 294–296° at atmospheric pressure.

2,4-Dimethoxybenzoic acid. Saponification of the methyl 2,4-dimethoxybenzoate with 10% methanolic potassium hydroxide for 2 hr. on the steam bath resulted in formation of a compound giving a new dark spot on the chromatostrip (R_f = 0.27), which when isolated crystallized from water as colorless needles, m.p. 108°. The material gave no ferric chloride reaction and was soluble in sodium carbonate.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.1; H, 5.49; OMe, 34.1. Found: C, 59.4; H, 5.54; OMe, 34.4.

Karrer *et al.*[12] have described the dimethoxybenzoic acid as having a melting point of 107°.

Acknowledgment. The authors gratefully acknowledge the assistance of L. M. White and G. Secor in obtaining the analytical data reported in this paper.

WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
AGRICULTURAL RESEARCH SERVICE
U. S. DEPARTMENT OF AGRICULTURE
ALBANY 10, CALIF.

(9) M. S. Rangaswami, *J. Ind. Chem. Soc.*, **16**, 160 (1939). (a) Mention of specific products does not constitute endorsement by the Department of Agriculture over others of a similar nature not mentioned. (b) All melting points were obtained on the Kofler block.

(10) N. Mauthner, *J. prakt. Chem.*, **159**, 36 (1941).

(11) H. P. Perkin and E. Schiess, *J. Chem. Soc.*, 159 (1904).

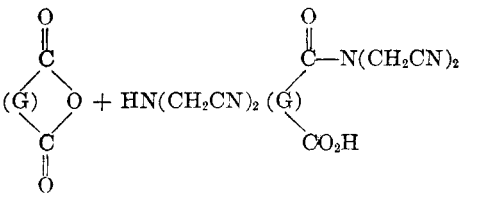
(12) G. Karrer, A. Rebmann, and E. Zeller, *Helv. Chim. Acta*, **3**, 261 (1920).

N,N-Bis(cyanomethyl)carboxamic Acids

JOHN W. LYNN

Received November 7, 1957

In a previous note[1] the synthesis of a series of *N,N*-bis(2-cyanoethyl)carboxamic acids was reported. This note describes the synthesis and properties of several analogous compounds, *N,N*-bis(cyanomethyl)carboxamic acids, which were prepared by the reaction of iminodiacetonitrile with cyclic anhydrides in an inert solvent.



(1) J. W. Lynn, *J. Am. Chem. Soc.*, **78**, 5829 (1956).

TABLE I

N,N-BIS(CYANOMETHYL)CARBOXAMIC ACIDS: $HO_2C—(G)—CON(CH_2CN)_2$

(G)	Formula	Yield, %	M.P.,[2] °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
—CH=CH—	$C_8H_7N_3O_3$	70	132–5	49.70	49.74	3.63	3.81	21.80	21.95
—CH=CCl—	$C_8H_6ClN_3O_3$	80	139–42	42.21	42.59	2.64	3.0	18.45	18.42
$—CH(C_8H_{15})CH_2—$	$C_{16}H_{23}N_3O_3$	95	Part. solid	63.0	61.8	7.54	7.60	13.76	12.34
	$C_{12}H_{13}N_3O_3$	70	147–9	58.3	58.0	5.26	5.50	17.0	16.6
	$C_{13}H_{13}N_3O_3$	68	128–32	60.2	60.4	5.02	5.26	16.2	16.18
	$C_{12}H_9N_3O_3$	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.

Acknowledgment. The author is grateful to Mr. A. Cooper for technical assistance.

RESEARCH DEPARTMENT
UNION CARBIDE CHEMICALS CO.
DIVISION OF UNION CARBIDE CORP.
SOUTH CHARLESTON 3, W. VA.

(2) All temperatures are uncorrected.

Preparation of Phenyldiazomethane[1,2]

PETER YATES AND BERNARD L. SHAPIRO[3]

Received November 11, 1957

Phenyldiazomethane 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 Jason[8] 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 phenyldiazomethane of *ca.* 40% purity.

As a result of our studies on the reaction of diazoketones with base[9] we have developed a novel and convenient method for the preparation of phenyldiazomethane 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 phenyldiazomethane 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 monohydrazone[10] and, when pure, may be stored in the cold for several months without deterioration, this is an attractive method for the preparation of ethereal phenyldiazomethane.

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:

$$C_6H_5CN_2COC_6H_5 + NaOH \longrightarrow C_6H_5CHN_2 + C_6H_5CO_2Na.$$

This mode of cleavage of an aliphatic diazo compound has previously been suggested by Wilds and Meader[11] 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*-chlorophenyldiazomethane 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*-chlorophenyldiazomethane with the aqueous basic medium, the reaction being favored

(1) Aliphatic Diazo Compounds. IV.
(2) Work supported by an institutional research grant from the American Cancer Society to Harvard University.
(3) Shell Foundation Fellow, 1955–1956.
(4) A. Hantzsch and M. Lehmann, *Ber.*, **35**, 897 (1902).
(5) E. A. Werner, *J. Chem. Soc.*, 1093 (1919).
(6) A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Res.*, **28B**, 683 (1950).
(7) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).
(8) C. D. Gutsche and E. F. Jason, *J. Am. Chem. Soc.*, **78**, 1184 (1956).
(9) B. L. Shapiro, Ph.D. Thesis, Harvard, 1957.
(10) C. D. Nenitzescu and E. Solomonica, *Org. Syntheses*, **Coll. Vol. II**, 496 (1943).
(11) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).