Oxidation of an aliquot of the crude product with potassium permanganate gave an acidic fraction and a neutral fraction. The acid, m.p. 100–127°, was free of halogen as indicated by the Beilstein test, and upon recrystallization from water melted at 117–118° (benzoic acid melts at 121°). The yield in the oxidation was 71%. The neutral material melted at 59–61° (lit.[44] for *p*-chlorobenzophenone 75.5–76°), but recrystallization raised the melting point to 66–69°, mixture melting point with authentic *p*-chlorobenzophenone 69–75°, yield 51%.

The oxidation product had the same infrared spectrum as authentic *p*-chlorobenzophenone and gave a 2,4-dinitrophenylhydrazone melting at 184–186° (lit.[45] 184–185°).

Acknowledgment.—This work is a contribution from the Radiation Project of the University of Notre Dame supported, in part, under Atomic Energy Commission contract AT(11-1)-38 and Navy loan equipment contract Nonr-06900. We are grateful to Dr. H. O. House for a critical reading of the manuscript. Mr. Marck Rerick performed the reductions of trimethylethylene oxide and Mr. Mark Mersereau coöperated in the reductions of 1,1-diphenylethylene oxide and 1,1-diphenyl-2-bromoethanol.

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[44] M. Kollarits and V. Merz, *Ber.*, **6**, 547 (1873).

[45] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1806 (1934).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

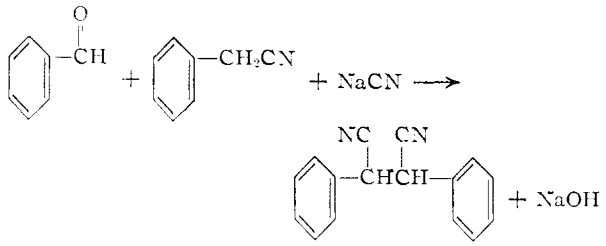
A New Method for Preparing Arylsuccinonitriles

BY R. B DAVIS[1]

RECEIVED OCTOBER 11, 1957

An aldehyde, an arylmethylene cyanide and an alkali metal cyanide react to form an arylsuccinonitrile. Some new arylsuccinonitriles have been prepared by this method.

Previously, the preferred method for preparing 2,3-diphenylsuccinonitrile was the method described by Lapworth and McRae[2] in which benzaldehyde benzyl cyanide were condensed to α-phenylcinnamonitrile using a base as a catalyst. Then hydrogen cyanide was added to the α-phenylcinnamonitrile to produce 2,3-diphenylsuccinonitrile. It has now been found that benzaldehyde, benzyl cyanide and sodium cyanide react to give this product in excellent yield.



Furthermore, it has been found that the reaction is general to the extent that other aldehydes and other arylmethylene cyanides may be used, and certain arylmethylene halides may be used in place of benzyl cyanide. Table I will serve to illustrate the versatility of the reaction.

The aldehyde, a slight excess of arylmethylene compound and the alkali metal cyanide are allowed to react in the presence of methanol or mixtures of methanol and water. Best results are obtained when about 2.5 to 3 moles of alkali metal cyanide per mole of the aldehyde are used. When the arylmethylene cyanide is produced *in situ* from an arylmethylene halide, a larger excess of the arylmethylene halide is employed as well as a corresponding larger excess of the alkali metal cyanide.

As the reaction proceeds alkali metal hydroxide is produced. During the early stages of the reaction, the base produced may actually be beneficial, but as its concentration increases, it may become detrimental. In one preparation of 2,3-diphenylsuccinonitrile, when a few grams of potassium hydroxide was added to the reaction mixture at the start and equivalent amounts of benzaldehyde and acetic acid gradually added, the product was obtained in improved yield.

Experimental[3]

Preparation of 2,3-Diphenylsuccinonitrile. A.—A mixture of 100 ml. of distilled water and 61.2 g. (1.25 moles) of sodium cyanide was warmed until nearly all the cyanide dissolved. Absolute, acetone-free methanol (400 ml.) was added, the mixture was heated to reflux, and 50 g. (0.425 mole) of benzyl cyanide was added all at once. A solution of 53 g. (0.5 mole) of benzaldehyde and 30 g. (0.256 mole) of benzyl cyanide was then added dropwise over 30 minutes with stirring at reflux. After the addition was completed, the reaction mixture was stirred at reflux for an additional 30 minutes. During the course of the reaction, a colorless solid precipitated and the liquid gradually took on a dark blue-green color. The reaction mixture was allowed to cool (2.5 hr.), was filtered with suction, and the solid was washed well with 75% methanol–water, with water, again with 75% methanol–water and then with ether. The colorless solid material weighed 89.5 g. (77% yield), m.p. 204–205°. A sample recrystallized from glacial acetic acid with practically quantitative recovery, as described by McRae and Bannard,[4] melted at 238–239° (lit.[4] 240–241° cor.).

B.—Following the same method as described in A, with the exception that 81 g. (1.25 moles) of potassium cyanide was used in place of the sodium cyanide, there was obtained 85.5 g. (74% yield) of product, m.p. 204–205°.

C.—A mixture of 100 ml. of distilled water, 61.2 g. (1.25 moles) of NaCN and 5 g. (0.089 mole) of potassium hydroxide was warmed until all solid had dissolved. Absolute, acetone-free methanol was added (400 ml.), the mixture heated to boiling and 50 g. (0.425 mole) of benzyl cyanide introduced all at once. This was followed by a mixture of 53 g. (0.5 mole) of benzaldehyde, 30 g. (0.256 mole) of benzyl cyanide and 30 g. (0.5 mole) of glacial acetic acid; the first 10 ml. was added over 20 minutes, precipitation then began and addition of the remaining aldehyde mixture was completed in 90 minutes. The mixture was refluxed for 15 minutes after addition and then cooled in an ice-bath with stirring. Filtration, washing of the solid with 250 ml. of 80% methanol, 300 ml. of H_2O at 60°, and another 250 ml.

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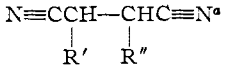
[1] Reverend Ralph B. Davis, C.S.C.

[2] A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 1709 (1922).

[3] Melting points are uncorrected.

[4] J. A. McRae and R. A. B. Bannard, *Org. Syntheses*, **32**, 63 (1952).

TABLE I



$$\underset{R'}{N{\equiv}CCH}{-}\underset{R''}{CHC{\equiv}N}^{a}$$

R	R″	Yield, %	M.p., °C.[b] Crude	Recrystd.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
C_6H_5	C_6H_5[c]	77–87	204–205	238–239				
C_6H_5	*p*-ClC_6H_4[d]	81	203	228–229	72.04	72.22	4.16	4.15
p-ClC_6H_4[e]	C_6H_5	60	193–195	226–228				
p-$OCH_3C_6H_4$	C_6H_5[f]	69	181–182	203–205[g]				
p-$OCH_3C_6H_4$	*p*-ClC_6H_4	54	186–188	222–224	68.80	68.58	4.41	4.48
p-ClC_6H_4[h]	*p*-ClC_6H_4	65	196–199	234–236	63.80	63.96	3.35	3.16
$C_7H_5O_2$[i]	C_6H_5	54	185–188	218–220	73.90	74.31	4.38	4.45
n-C_3H_7	C_6H_5	30	88–94	94–97	78.75	78.98	7.12	7.16[j]
p-(*i*-C_3H_7)C_6H_4	C_6H_5	58	197–200	204–206	83.18	83.37	6.61	6.56[k]

[a] R′ is from an aldehyde, $R'\overset{O}{\overset{\|}{C}}H$. R″ is from an arylmethylene cyanide, $R''CH_2CN$. [b] Melting points are uncorrected. [c] Benzyl chloride in place of benzyl cyanide gave 80% yield. [d] *p*-Chlorobenzyl chloride in place of *p*-chlorobenzyl cyanide gave 42% yield. [e] The reagents were mixed at room temperature. The mixture was then heated slowly to 55°. [f] Benzyl chloride in place of benzyl cyanide gave 65% yield. [g] Lit. value 204°; J. A. McRae and A. S. Townshend, *C. A.*, **29**, 1078 (1935). [h] Reaction temperature 45–55°. [i] 3,4-Methylenedioxyphenyl. [j] Nitrogen, calcd. 14.13, found 14.20. [k] Nitrogen, calcd. 10.21, found 10.25.

of 80% methanol and drying under vacuum gave 101 g. (87%) of solid, m.p. 202–205°, recrystallized from acetic acid, m.p. 235–237°.

D.—A mixture of 111 g. of sodium cyanide, 100 ml. of water and 500 ml. of absolute methanol was heated to gentle reflux. Then 40 g. of benzyl chloride was added dropwise over 15 minutes with vigorous stirring. A mixture of 90 g. of benzyl chloride and 53 g. of benzaldehyde was added over 35 minutes at gentle reflux with vigorous stirring.[5] The reaction mixture was refluxed for one hour with vigorous stirring, allowed to cool and was filtered. The solid was washed well with 70% methanol, water, 70% methanol and ether, and then air-dried. The solid weighed 93 g. (80% yield), m.p. 203–206°, recrystallized from acetic acid, m.p. 235–236°.

Preparation of 2-Phenyl-3-propylsuccinonitrile.—To a mixture of 50 ml. of water, 49 g. of sodium cyanide, 250 ml. of absolute methanol and 15 g. of benzyl cyanide, heated to 35–40°, was added with stirring over 4 hours a mixture of 24 g. of benzyl cyanide, 21.6 g. of butyraldehyde and 200 ml. of absolute methanol. The reaction mixture was then heated at 35–40° with stirring for one additional hour. Two liters of water was added and the mixture extracted four times with 300-ml. portions of ether. The combined extracts were washed with water and dried over potassium carbonate. The ether was removed by distillation, 200 ml. of fresh ether was added, and the mixture was placed in the refrigerator overnight, during which time solid precipitated. The mixture was filtered and the solid washed with 70% methanol. The solid, 18 g. (30% yield), melted at 88–94°, recrystallized from ethanol, m.p. 94–97°.

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[5] The reaction is exothermic—caution. During the course of the reaction the heating mantle was removed most of the time, the reaction heat maintained reflux. After addition was complete, heat was applied.

[CONTRIBUTION FROM THE PHYSIOLOGY DIVISION, CHEMICAL WARFARE LABORATORIES]

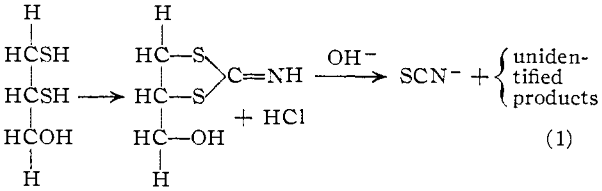
Formation of Thiocyanate Ion through Neighboring Group Displacement Reactions

BY JOEL R. SIEGEL[1] AND DAVID H. ROSENBLATT

RECEIVED AUGUST 8, 1957

A general mechanism is proposed for the release of thiocyanate ion from vicinal and geminal aliphatic dithiocyanates, β-mercaptoaliphatic thiocyanates and 2-imino-1,3-dithiolanes on treatment with base. The series of reactions whereby the aqueous solution of a vicinal dithiol is treated with cyanogen chloride and then made basic to release thiocyanate ions is discussed in the light of the general mechanism.

The interest of these laboratories in the chemistry of 2,3-dimercapto-1-propanol (BAL), which is used as an antidote for arsenical and heavy metal poisoning, occasioned an inquiry into the nature of the initial steps in Aldridge's method[2] for determining aliphatic vicinal dithiols. This method entails estimation of the thiocyanate ion liberated when a vicinal dithiol is treated with cyanogen chloride and made alkaline; it is rather specific and very sensitive, but tedious, exacting and time-consuming. It occurred to us that there might be found a simpler, if less sensitive, means of estimating the postulated intermediate, 2-imino-4-hydroxymethyl-1,3-dithiolane,[2] if additional evidence should confirm Aldridge's hypothesis, namely



(1)

Although simple organic thiocyanates commonly react with base to give mercaptide ions and cyanate, with disulfides as end products,[3] examination of

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[1] Esso Research and Engineering Co., Linden, N. J.

[2] W. N. Aldridge, *Biochem. J.*, **42**, 52 (1948).

[3] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).